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XXXV.—THE DECOMPOSITION OF NITRIC ETHERS BY ALKALINE SOLUTIONS.

BY W. G. MIXTER.

In an examination of a number of high explosives containing some form of gun-cotton or nitrated woody fiber, an attempt was made to prove qualitatively the presence of cellulose nitrate. The substance tested was digested with an alkali sulphide to convert the nitrate into cellulose, then an excess of hydrochloric acid was added, and the mixture boiled for some time to change the cellulose into a sugar having a reducing action on Fehling's solution. The method was not satisfactory, as it was found that gun-cotton and a number of other nitric ethers reduce Fehling's solution directly and without previous treatment with a reducing agent. This observation led to experiments on the decomposition of nitric ethers by alkaline solutions—a line of investigation in which a considerable amount of work has already been done, and in which so much still remains obscure.

Ethyl Nitrate.

According to Millon,[1] ethyl nitrate is decomposed by alcoholic potash, with separation of potassium nitrate free from nitrite. The writer also has found the product to be free from nitrite. Oxalic acid was not formed in the reaction. Ethyl nitrate was heated

[1] Ann. chim. phys. [3] **8**, 233.

with Fehling's solution,[1] and also with addition of alcohol to dissolve the ether, and in both experiments there was no reduction of copper.

Ethylene Nitrate.

According to Champion,[2] this ether is decomposed by a boiling solution of potassium hydroxide, with formation of ethylene alcohol and potassium nitrate. The decomposition is, however, more complex and not simply a saponification, as the following results show: Ethylene nitrate and concentrated potassium hydroxide were heated together on a water-bath; the change was slight, but on addition of alcohol a violent reaction set in, the solution becoming dark red. A portion of the residue after expelling the alcohol from the solution and adding sulphuric acid, gave off red fumes, showing the presence of considerable nitrite. From the remainder of the residue nitrate was separated, but oxalic acid was not detected. In another experiment ethylene nitrate was decomposed by a boiling solution of potassium hydroxide.[3] The solution obtained on addition of acetic acid and warming gave off carbon dioxide, which formed a considerable precipitate with barium hydroxide. In the product of the decomposition of ethylene nitrate by caustic potash, cyanogen and ammonia were not detected, nor was it found what compounds of carbon other than carbon dioxide were formed. Ethylene nitrate does not reduce Fehling's solution.

A mixture of ethylene nitrate with a solution of barium hydroxide and a little alcohol was heated to boiling; a precipitate slowly formed, consisting in part of barium oxalate. From the solution filtered from the precipitate after removing the barium hydroxide by means of carbon dioxide, a sticky red residue containing nitrite was obtained.

Nitro-glycerin.

It is stated in handbooks and dictionaries of chemistry, the new edition of Watts excepted, that nitro-glycerin and caustic potash react to form glycerin and potassium nitrate. This is based on a

[1] The Fehling solution used in all the experiments was made of 173 grams of sodium-potassium tartrate and 125 grams of potassium hydroxide dissolved in water to make 500 cc., and 34.6 grams of crystallised copper sulphate in 500 cc. of water. The two solutions were kept separate until used.

[2] Comptes rend. **73**, 571.

[3] The potassium hydroxide used in this and similar experiments was made from metallic potassium and was free from carbonate.

statement by Williamson[1] and also on an investigation by Railton,[2] both of whom obtained glycerin and potassium nitrate, but made no mention of other products of the decomposition. Later Dr. Matthew Hay[3] made a very good investigation of the action of caustic potash on nitro-glycerin, and showed that the reaction is very complex, and not a simple saponification with formation of glycerin. He found when nitro-glycerin was decomposed by alcoholic potash that two-thirds of the $—NO_3$ of the nitro-glycerin was reduced to nitrous anhydride, N_2O_3, and that oxalic acid, a little ammonia and acetic acid were formed. The last may have resulted from oxidation of the alcohol in alkaline solution. Glycerin was not satisfactorily identified as one of the products of the decomposition. The experience of the writer confirms Hay's results in this, that oxalic and nitrous acids and a little ammonia are formed, and that in addition carbon dioxide, nitric acid, and traces of glycerin and cyanogen are among the products of the decomposition of nitro-glycerin by aqueous caustic potash. Organic acids other than oxalic are apparently formed in abundance, but attempts to isolate them have failed. Among the products of the decomposition of nitro-glycerin, glycerose, which is formed by oxidation of glycerin, was tested for with phenylhydrazine, but was not found. The experiments were as follows:

Commercial glycerin, not very pure, was mixed slowly with red fuming nitric acid, cooled by a current of water at 5°, and then oil of vitriol was added gradually. After half an hour the mixture was poured into cold water, and the nitro-glycerin obtained was washed with a solution of sodium carbonate, and finally with water, and dried *in vacuo* over caustic potash. It was colorless, free from acid, and gave on combustion by the absolute method 18.51 per cent. of nitrogen, theory requiring 18.50. This preparation was designated as "A." Another preparation called "B" was made from a purer glycerin known as Price's, and 18.35 per cent. of nitrogen was found in it.

Eight grams of preparation "A" and 50 cc. of potassium hydroxide (density, 1.33) were heated together on a water-bath for some hours until the nitro-glycerin disappeared. A crystalline meal separated, which increased on cooling the mixture. It was filtered off and washed once with cold water, and proved on

[1] Proc. Royal Soc. **7**, 130. [2] J. Chem. Soc. **7**, 222.
[3] Trans. Royal Soc. Edin. (1882-3) **32**, 67.

analysis to be potassium oxalate. The filtrate from it, on addition of sulphuric acid, gave off nitrous fumes, but glycerin was not detected. Five grams of preparation "B" were decomposed with potassium hydroxide (density, 1.36), and the ammonia evolved was converted into ammonium chloride, which weighed 0.119 gram, showing that $\frac{1}{30}$ of the nitrogen of the nitro-glycerin had been converted into ammonia. Oxalic acid was estimated as calcium oxalate in $\frac{1}{8}$ of the solution, and the result showed that $\frac{1}{18}$ of the carbon of the nitro-glycerin was converted into oxalic acid. From the remaining $\frac{5}{8}$ of the solution potassium nitrate was obtained, but no glycerin.

In order to test more thoroughly for glycerin in the products of decomposition, much larger quantities of nitro-glycerin were used. In one experiment 24 grams of preparation "A" were decomposed by 115 cc. of potassium hydroxide (density, 1.4), and the salts which separated were removed. Carbon dioxide was then passed into the solution as long as hydrogen-potassium carbonate separated, and this was filtered off and washed with alcohol. The filtrate and washings were evaporated until a viscid mass remained, which was shaken up with alcohol; the solution poured off from the undissolved salts was evaporated, and the residue left was also extracted with alcohol. This last solution yielded a viscid product which gave a feeble but distinct odor of acrolein when heated with phosphorus pentoxide. 32 grams of preparation "B," treated as just described, also reacted for a trace of glycerin. In order to test the method employed, 10 grams of potassium nitrite, 2 grams of oxalic acid, and 0.5 gram of glycerin were added to a solution of caustic potash, and the mixture was treated as above described. Glycerin was found in much larger quantity than in the foregoing tests.

Nitro-glycerin of preparation "A" was decomposed by an aqueous solution of pure potassium hydroxide, and the solution was found to give off carbon dioxide on the addition of an acid. No gas was obtained when nitro-glycerin was decomposed *in vacuo* by pure concentrated potassium hydroxide, and the solution reacted for a trace of cyanogen.

Nitro-glycerin dissolves in a hot Fehling solution, and cuprous oxide continues to separate long after the oily drops of the ether have disappeared, showing that reducing compounds are gradually formed by the action of the alkali. The reducing bodies are,

however, decomposed by the alkali, for when nitro-glycerin is first dissolved in concentrated potassium hydroxide and Fehling's solution then added, no reduction occurs. But if the decomposition is effected by barium hydroxide, the reducing compound is not destroyed. 30 grams of nitro-glycerin were added to a boiling solution of 150 grams of barium hydroxide in 600 cc. of water, and the boiling was continued half an hour. Ammonia came off and a reddish precipitate separated, which was washed with water and finally with alcohol to remove any adhering nitro-glycerin. This precipitate reduced Fehling's solution, and gave off ammonia when heated with lime. It was treated with acetic acid, and the undissolved portion proved on analysis to be barium oxalate. The acetic acid solution was evaporated until a crystalline crust formed, which gave analytical results indicating a mixture, doubtless containing oxalate. In another experiment the precipitate obtained as before was digested with the amount of sulphuric acid required to remove the barium. The filtrate from the barium sulphate did not yield crystals on evaporation, and when treated with phenyl-hydrazine hydrochlorate, sodium acetate and acetic acid, a dark-red sticky precipitate formed, which was apparently a product of the decomposition of phenyl-hydrazine. The filtrate from the precipitate formed in the reaction between the barium hydroxide and nitro-glycerin contained nitrite and nitrate and organic matter.

Nitro-mannite.

30 grams of this compound were gradually added to a boiling, clear solution of 100 grams of barium hydroxide in a liter of water, and the boiling was maintained for an hour. No ammonia was detected in the escaping steam. The decomposition of the nitro-mannite was accompanied by the formation of a red granular precipitate, which was filtered off and thoroughly washed with hot water. It was evidently a mixture, as it contained barium oxalate and reduced Fehling's solution. It was treated with a slight excess of dilute sulphuric acid, and to the filtrate from the barium sulphate, phenyl-hydrazine hydrochlorate, sodium acetate, and acetic acid were added to separate, if possible, any ketonic acid or compound which reduces copper. A dark-red precipitate formed at once, which increased on warming and standing. It was insoluble in alcohol, the solution yielding only a tarry mass when evaporated. The filtrate from the phenyl-hydrazine product, on evaporation and cooling, deposited crystals of phenyl-hydrazine oxalate.

The filtrate from the red precipitate produced by the reaction between nitro-mannite and barium hydroxide, was treated with carbon dioxide to remove barium hydroxide. The solution filtered from the barium carbonate contained barium nitrite in abundance, and also nitrate. It did not reduce Fehling's solution, nor yield a precipitate with lead acetate. It left a residue on evaporation, which deflagrated, thus showing the presence of carbon compounds.

Nitro-mannite is easily decomposed by a hot solution of potassium hydroxide; if the solution be concentrated, oxalic acid is formed. When a very dilute solution of the alkali was used, no oxalic acid was detected. In one experiment, about $\frac{1}{10}$ of the carbon of nitro-mannite was converted into carbon dioxide, when the ether was decomposed by concentrated potash solution. The product of the decomposition of nitro-mannite by a strong solution of potassium hydroxide does not reduce Fehling's solution; but if the alkali be dilute, the solution has a slight reducing action. When, however, nitro-mannite is added to Fehling's solution, there is considerable reduction. Two estimations were made with 0.5 gram of nitro-mannite and 50 cc. of Fehling's solution, and, after boiling three-quarters of an hour, 0.1356 and 0.130 gram of metallic copper respectively were obtained. After boiling an hour longer, the total amount of copper precipitated was 0.196 and 0.199 gram respectively.

Cellulose Nitrates.

The action of caustic potash on pyroxylin has been investigated by Béchamp[1] and by Eder.[2] The former states that if pyroxylin be heated with a solution of caustic potash, and the action be stopped just before a stage in the decomposition is reached where acids fail to produce a precipitate, and the solution is exactly neutralised with dilute sulphuric acid, it is possible to prove the formation of a sugar. For this, the solution is evaporated on a water-bath and extracted with hot alcohol. The alcohol leaves a saline residue of sulphate, nitrate and nitrite, and holds in solution a certain quantity of sugar. The sugar product was fermented and alcohol obtained. The writer has repeatedly sought by means of phenyl-hydrazine for a sugar, and found none among the products of decomposition of pyroxylin, by dilute solutions of caustic potash. The pyroxylin used was a commercial article,

[1] Ann. chim. phys. [3], **46**, 338. [2] Ber. d. chem. Ges. **13**, 169.

soluble in ether-alcohol, and had the composition of cellulose tetranitrate, $C_{12}H_{10}(NO_3)_4O_{10}$, doubtless containing tri- and penta-nitrates. The method employed was as follows: 28 grams of pyroxylin were placed in 500 cc. of water, to which from 40 to 70 cc. of potassium hydroxide (density, 1.4) had been added. The mixture was heated until most of the pyroxylin had dissolved, then cooled, and a slight excess of either sulphuric or hydrochloric acid added, an excess being required to completely precipitate a small quantity of undecomposed cellulose nitrate. The solution was filtered, exactly neutralised with potassium hydroxide, and evaporated nearly to dryness on a water-bath. The saline residue, after washing two or three times with alcohol, which removed but little organic matter, blackened on ignition and reduced Fehling's solution. It was dissolved in a small quantity of water, and phenyl-hydrazine hydrochlorate, sodium acetate and acetic acid were added. A yellow precipitate separated, which turned red on warming the solution, and was apparently a decomposition-product of phenyl-hydrazine. In one experiment, a sparingly soluble potassium salt, not the oxalate, was obtained. Repeated attempts to prepare more of the salt failed.

While working with phenyl-hydrazine, as just described, the writer's hand was repeatedly blistered by vapors and by solutions. No poisonous effects were, however, noticed after experimenting with phenyl-hydrazine and the products of decomposition by alkalies of nitric ethers other than pyroxylin. At some future time the writer will endeavor to identify the poisonous compound.

Eder[1] states that alkalies decompose pyroxylin with formation of nitrites and nitrates, but little nitrate being formed when dilute alcoholic potash is used. Béchamp[1] found that glucic and apoglucic acids resulted from prolonged action of concentrated potash. The writer finds that oxalic and carbonic acids are formed when pyroxylin is decomposed by a strong solution of caustic potash, and the product does not reduce Fehling's solution. A solution of pyroxylin in dilute caustic potash has, however, some reducing action.

Pyroxylin dissolves quickly in a hot Fehling solution, and cuprous oxide separates at once, but the reduction continues for a long time. In two estimations, using for each 0.5 of soluble pyroxylin and 50 cc. of Fehling's solution and boiling three hours,

[1] Loc. cit.

0.375 and 0.365 gram respectively of copper were precipitated as cuprous oxide. 0.5 gram of another sample of pyroxylin gave 0.4 gram of copper on boiling an hour, and 0.44 gram at the end of two hours, 50 cc. of Fehling's solution being used.

In another test with 0.5 gram of the same sample, and 50 cc. of Fehling's solution diluted with its bulk of water, only 0.25 gram of copper was precipitated, and no further reduction occurred after boiling an hour. There was an undetermined error in using Fehling's solution undiluted, as it deposited a small amount of cuprous oxide when boiled for some time. A specimen of gun-cotton which was nearly pure cellulose hexanitrate reduced about half as much copper from an undiluted Fehling's solution as pyroxylin under like conditions.

Other Nitric Ethers and Reducing Compounds.

The following substances are converted by concentrated nitric acid into compounds which precipitate cuprous oxide from Fehling's solution: Pinite, woody fiber, gum arabic, gum tragacanth, balsam of tolu, glycogen, starch and saccharose. The nitrated products of blood-albumen, hard-boiled white and yelk of egg, caoutchouc, tartaric acid, beeswax and tallow were found to be without reducing action.

Summary.

Ethyl nitrate and potassium hydroxide react to form ethyl alcohol and potassium nitrate, and there is no reduction of the NO_2-group or oxidation of the ethyl-group. Ethylene nitrate is decomposed by concentrated alkaline solutions with formation of carbonic, oxalic, and nitrous acids, part of the oxygen of the NO_3-groups oxidising the hydrocarbon radicle. Nitro-glycerin, nitro-mannite, and pyroxylin exhibit a similar deportment, and in addition yield other organic acids and products which have a reducing action on Fehling's solution.

XXXVI.—RESEARCHES ON THE ISO-ANILIDES.

By W. J. Comstock and H. L. Wheeler.

In the first part of this paper we shall describe experiments which show that the sodium and silver salts of form-α-naphthalide and of metanitro-formanilide show, in their behavior towards methyl iodide, the same difference that has been found in the salts

of other aromatic formyl compounds. The second part contains a description of experiments made with the iso-anilides, showing that they react with secondary amines, both fatty and aromatic, and with cyan-amide.

Gattermann[1] made the interesting observation that nitro-para-acetoluide occurs in two modifications, and suggested the possibility that these two modifications might correspond to the forms containing the two groups —N=C(OH)— and —NH—CO—. It seemed possible that in the case of nitro-formanilide—whose salts behave towards methyl iodide as if they had the structures —NNa—CO— and —N=C(OAg) respectively—these two modifications might be obtained by decomposing the salts. But we were able to obtain but a single modification of the meta-nitro-formanilide in this way. The decomposition of both salts by dry hydrochloric acid in presence of dry ether and in presence of dry chloroform; the decomposition of the silver salt by dry hydrogen sulphide in presence of dry ether; and the decomposition of the sodium salt by moist carbonic acid in presence of ether; all gave products having the same melting-point. In each case, on evaporating the solution at ordinary temperature, the crystals had exactly the same appearance under the microscope, consisting of tufts of extremely fine, hair-like, bent needles. Under these conditions we could not, however, obtain crystals that were fitted for crystallographical or optical examination.

Silver salt of form-α-naphthalide.—Prepared by adding gradually the theoretical quantity of silver nitrate in 50 per cent. alcoholic solution to the aqueous alcoholic solution of sodium hydroxide and the formyl compound. The silver salt separates as a voluminous gray precipitate, amorphous and sensitive to light, insoluble in water.

	Found.	Calculated.
Ag	39.14	38.84

Methyl-iso-form-α-naphthalide.—Prepared by treating the dry silver salt with methyl iodide in presence of dry ether, this compound is obtained as a heavy oil, having a strongly fishy odor, and boiling at ordinary pressure, with noticeable decomposition at 306°–308°.

	Found.	Calculated.
C	77.8	77.7
H	5.9	6.0

[1] Ber. d. chem. Ges. **23**, 1733.

It shows the same behavior towards water, dilute acids and primary amines, that methyl-iso-formanilide does.

Di-α-naphthyl-formamidine.—Formed by treating the above-described ether with α-naphthylamine, and recrystallising from hot benzene. It forms colorless plates, which melt at 199°, and are moderately soluble in alcohol, ether and benzene, insoluble in ligroin. Does not dissolve in cold, dilute mineral acids.

	Found.	Calculated.
C	85.2	85.1
H	5.5	5.4
N	9.4	9.5

Phenyl-α-naphthyl-formamidine, prepared by treating methyl-iso-form-α-naphthalide with aniline, is purified by dissolving in benzene and precipitating with ligroin. Its melting-point is 142°. It is soluble in alcohol, ether and benzene, difficultly soluble in ligroin.

	Found.	Calculated.
C	83.3	82.9
H	5.8	5.7
N	11.3	11.4

The basic properties are much more strongly marked than in the case of the dinaphthyl-amidine.

The reaction of methyl iodide with the sodium salt of form-α-naphthalide is not a satisfactory operation, owing to the properties of the methyl-naphthyl-amine. However, by Hepp's method, we obtained the base corresponding to that described by Landshoff.[1] An attempt to purify it by means of the nitrosamine was a failure, as nitrous acid seemed to have a more complicated action, and left a most uninteresting resinous product. However, by means of the acetyl compound described by Landshoff, we were able to identify the secondary amine.

Meta-nitro-formanilide.—This is easily prepared by boiling meta-nitraniline with an excess of pure formic acid, adding water and recrystallising from hot water, alcohol or benzene. It melts at 134°. It is soluble in hot water, alcohol and benzene; difficultly soluble in ether and ligroin.

	Found.	Calculated.
C	50.6	50.6
H	3.9	3.6

[1] Ber. d. chem. Ges. **11**, 638.

Sodium meta-nitro-formanilide.—To prepare the sodium salt, the best method is to dissolve the theoretical quantity of sodium in the smallest possible quantity of pure, dry methyl alcohol, and add it to the formyl body, which has been moistened to a paste with methyl alcohol. The lemon-yellow salt which is formed is readily soluble in methyl alcohol, and should be washed thoroughly with dry ether. A sodium estimation in the salt thus prepared gave Na = 12.1 per cent. (calculated, Na = 12.2 per cent.). Exposed to the air the salt gradually absorbs carbonic acid, and is finally completely converted into sodium carbonate and the formyl compound. If in preparing the sodium salt the methyl alcohol is not thoroughly washed out by ether, the lemon-yellow salt gradually changes into a mass of orange-colored needles, which, dried over sulphuric acid, gave Na = 10.1 per cent. The theoretical percentage for the sodium salt with one mol. CH_3OH is Na = 10.45. The same orange-colored needles are obtained when the alcoholic solution is concentrated. On adding water to the alcoholic solution of the salt, the free formyl compound is precipitated.

Action of methyl iodide on the sodium salt.—Methyl iodide reacts but slowly with the sodium salt when warmed on the water-bath in a flask fitted with an inverted condenser; nevertheless the reaction can be made to take place in this way if the heating be continued for some days, care being taken to exclude moisture and carbonic acid.

The reaction is finished when a specimen of the mixture no longer shows an alkaline reaction. The reaction takes place in a very few hours when conducted in a sealed tube at 100°. In either case, by crystallising from alcohol, the nitro-formyl-methyl-aniline can be obtained in long needles, having a slight yellowish tinge and melting at 70°–71°.

	Found.	Calculated.
C	53.0	53.3
H	4.5	4.4

The meta-nitro-monomethyl-aniline prepared from the pure formyl compound melted at 67°, and the nitrosamine, which we obtained perfectly white, melted at 76°. Nölting and Stricker[1] gave 65°–66° and 68°–70° as the melting points of these two compounds.

Silver meta-nitro-formanilide.—The silver salt can be prepared

[1] Ber. d. chem. Ges. **19**, 548.

in aqueous-alcoholic solution in the same manner as silver formanilide. It is amorphous, and, when first precipitated, colorless. It can be washed with hot water.

	Found.	Calculated.
Ag	39.8	39.3

Meta-nitro-methyl-iso-formanilide is prepared by treating the dry silver salt with methyl iodide diluted with ether. On fractioning at a pressure of 21 mm., the iso-anilide was obtained, boiling at 172°–173°; temperature of bath, 190°. The compound solidifies in the receiver to a mass of long, slender, light-yellow needles, melting at 45°.

	Found.	Calculated.
C	53.5	53.3
H	4.5	4.4
N	15.8	15.6

The ether reacts with primary amines, as do the others thus far described, but the tendency to form the amidine in presence of water is not so marked as in the case of the non-substituted iso-anilides. Treated with dilute hydrochloric acid, for instance, the salt of meta-nitraniline is obtained at once.

Dinitro-diphenyl-formamidine, $CH\begin{matrix}=N.C_6H_4.NO_2\\ \diagdown NH.C_6H_4.NO_2\end{matrix}$.—A mixture of the theoretical quantities of the iso-anilide and meta-nitraniline, heated up slowly on a bath, remained liquid from 50° to about 110°, at which temperature the mass became solid. On recrystallising from alcohol, the amidine was obtained in small yellow hair-like needles, melting at 195°–196°. A combustion of the substance dried at 130° gave the following results:

	Found.	Calculated.
C	54.9	54.5
H	3.6	3.5

The compound is soluble in alcohol, ether, chloroform, and acetone; insoluble in ligroin.

Mono-nitro-diphenyl-formamidine, $CH\begin{matrix}=N.C_6H_4.NO_2\\ \diagdown NH.C_6H_5\end{matrix}$. — On adding the theoretical quantity of aniline to the fused ether, the mixture solidifies in a few minutes, and when crystallised from absolute alcohol the amidine is obtained in long yellow prisms which melted at 145°.

	Found.	Calculated.
C	64.8	64.7
H	4.7	4.6

The following experiments will serve to show that the iso-anilides react with secondary amines, fatty and aromatic, forming trisubstituted amidines:

Diethyl-phenyl-formamidine, $CH\begin{matrix}//N.C_6H_5\\ \backslash N.(C_2H_5)_2\end{matrix}$.—A mixture of methyl-iso-formanilide and a slight excess of diethyl-amine was boiled in a flask fitted with an inverted condenser for about two hours, and then distilled at ordinary pressure. Practically the entire quantity came over between 265° and 275°. On redistilling, a nearly colorless oil was obtained, boiling at 273°–275°. There was, however, a noticeable decomposition, and the compound had a strongly alkaline odor. Converted into the gold double-salt and recovered, the amidine is colorless and odorless. The gold double-salt is difficultly soluble in water, easily soluble in alcohol, and crystallises in small lemon-yellow plates when water is added to the alcoholic solution; the plates melt at 147°. After drying over sulphuric acid *in vacuo*, its analysis gave the following results:

	Found.	Calculated for $CH\begin{matrix}//N.C_6H_5\\ \backslash N.(C_2H_5)_2\end{matrix}.HCl + AuCl_3$.
C	25.9	25.6
H	3.5	3.3
N	5.4	5.4
Au(=196.6)	37.9	38.1

Methyl-diphenyl-formamidine, $CH\begin{matrix}=N.C_6H_5\\ \backslash N<CH_3\\ \quad\quad C_6H_5\end{matrix}$.—A mixture of monomethyl-aniline and methyl-iso-formanilide was allowed to stand at ordinary temperature for some days, and, after having been warmed on the water-bath a short time, was distilled under diminished pressure: an excellent yield of the amidine was obtained. The substance is a heavy yellowish oil, boiling at 214° under 22 mm. pressure; temperature of bath, 260°.

	Found.	Calculated.
C	79.6	80.0
H	6.7	6.7
N	13.5	13.3

The gold double-salt is difficultly soluble in water, and when water is added to the alcoholic solution crystallises in gold-colored

plates which melt at 145°. A gold estimation in the air-dried salt gave Au = 35.7 per cent.; calculated for the anhydrous salt, Au = 35.7 per cent.

Action of Cyan-amide on the Iso-anilides.

Cyan-phenyl-formamidine, $CH\begin{matrix}=N.C_6H_5\\ \diagdown N.H.CN\end{matrix}$.—When an ethereal solution of cyan-amide and methyl-iso-formanilide is allowed to stand at ordinary temperature, it soon begins to deposit a crystalline crust, the separation of which is practically complete in 24 hours, unless the solution is very dilute. The new compound, after washing with ether, can be recrystallised from hot water or alcohol, in both of which it is quite soluble. From alcohol it separates in long, flat, colorless prisms; from hot water, in long needles. Its melting-point is 138°. Its analysis corresponds to the formula $C_8H_7N_3$, and its structure is in all probability represented by the formula $CH\begin{matrix}=N.C_6H_5\\ \diagdown N.H.CN\end{matrix}$.

	Found.	Calculated.
C	66.0	66.2
H	5.0	4.8
N	29.0	29.0

Cyan-para-tolyl-formamidine.—Cyan-amide reacts with methyl-iso-form-para-toluide in ethereal solution in the same way that it does with the iso-anilide. Recrystallised from alcohol the new body is obtained in long, well-developed prisms which melt at 176°–177°.

	Found.	Calculated.
C	68.0	67.9
H	5.7	5.6
N	26.3	26.4

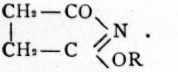
XXXVII.—ON THE PREPARATION OF OXYGEN-ETHERS OF SUCCINIMIDE FROM ITS SILVER SALT.

By W. J. Comstock and H. L. Wheeler.

The action of ethyl iodide on silver succinimide has already been tried by Menschutkin,[1] as well as by Landsberg,[2] in the

[1] Ann. Chem. (Liebig) **162**, 170. [2] Ibid. **215**, 211.

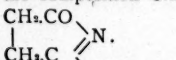
course of his extended investigation on the imides of dibasic acids. Both investigators state that they obtained only silver iodide and regenerated succinimide. Comstock and Kleeberg[1] found that by treating dry silver succinimide with methyl iodide, at most a trace of succinimide was regenerated; but they did not obtain the resulting compound in a pure state. That it was not the well known methyl succinimide, *i. e.*, the nitrogen-ether of succinimide, was shown by the fact that it reacted with aniline, with the formation of the base to be described later. We have taken up the work at this point and succeeded in preparing in a state of purity the ethyl and propyl compounds resulting from the action of the corresponding iodides on silver succinimide. These compounds were found to be isomeric with the nitrogen ethers of succinimide, and have, without doubt, the structure



We have not attempted to prepare the corresponding methyl-derivative, as its boiling-point was found by Kleeberg to be too near that of the nitrogen-ether to allow a separation by fractional distillation, in case any nitrogen-ether should be formed in the reaction. It is absolutely essential in preparing the oxygen-ethers, to exclude all moisture, even after the reaction is over, as the pure bodies form succinimide when exposed to moist air:

$$C_4H_4NO_2R + H_2O = C_4H_5NO_2 + ROH.$$

This ready formation of succinimide from the oxygen-ethers explains Landsberg's failure to obtain anything but silver iodide and succinimide when he allowed ethyl iodide to act on the dry silver salt in presence of dry benzene. We have found that the oxygen-ethers are formed in presence of dry benzene, ether or chloroform, the last being used in conducting the reaction with larger quantities. The formation of the oxygen-ether can readily be detected after filtering from the silver iodide, by evaporating the solvent and adding a few drops of aniline. The base formed has the composition $C_{10}H_{10}N_2O$, and has without doubt the formula



[1] Ber. d. chem. Ges. **23**, 2274; This Journal **12**, 493.

Succinimide is thus placed in the category with formanilide and other formyl compounds of primary aromatic amines, since it was shown by Landsberg that the alkaline salts give the nitrogen-ethers when treated with alkyl iodides. We were also able to show that in each case a small quantity of the nitrogen-ether had been formed from the silver salt. This was done by decomposing the ethers with a solution of potassium hydroxide, and showing the presence of a primary amine by the iso-nitrile reaction. This formation of a small quantity of nitrogen-ether from the silver salt renders the assumption of a different structure for the sodium and silver salts less satisfactory, as in that case refuge must be taken in the assumption of a molecular rearrangement at low temperature. We have attempted to find experimental evidence that might throw more light on this interesting subject, but as our results have been thus far negative, we present the definite experimental results already obtained and postpone the discussion of the theory till a future date.

Oxygen-ethyl-succinimide.—Silver succinimide dried to a constant weight at 100° was allowed to stand for several weeks at ordinary temperature with the theoretical quantity (1 mol.) of ethyl iodide diluted with two to three times its weight of dry chloroform. After filtering off the silver iodide and washing with more dry chloroform, the chloroform was distilled off on the water-bath, and the dark, oily residue distilled under diminished pressure. A second distillation yielded the oxygen-ether as a colorless oil, boiling at 144°–146° under a pressure of 20 mm., the temperature of the bath being 190°. The compound decomposes when boiled at ordinary pressure, and even at 20 mm. a slight decomposition can be noticed. Analysis gave results agreeing with the theory.

	Found.	Calculated for $C_6H_9NO_2$.
C	56.62	56.69
H	7.11	7.09

On adding aniline the mixture solidifies at once, and with noticeable evolution of heat if more than a few drops are used in the reaction. When exposed to moist air the pure ether gradually solidifies, forming succinimide, which shows the correct melting-point without recrystallisation. In order to test for the presence of the nitrogen-ether, a small quantity of the chloroform solution, representing about six to eight grams of silver salt freshly filtered from silver iodide, was treated with water and allowed to stand

several hours after vigorous shaking. The chloroform was then distilled off, the aqueous solution distilled with potassium hydroxide, and an examination for primary amine made in the way described under the propyl-ether. The presence of a primary amine was shown beyond doubt, therefore some nitrogen-ether had been formed in the reaction. If the nitrogen-ether is formed by molecular rearrangement from the oxygen-ether, that rearrangement must take place in this case at ordinary temperature, as the oxygen-ether must have been completely converted into succinimide by the action of the water before any heat was applied. The nitrogen-ethyl-ether, which was prepared for comparison according to Menschutkin, boiled at 235° at 763 mm. pressure (Menschutkin gives 234°), and at 20 mm. showed the boiling-point 122°; temperature of bath, 155°. It does not react with aniline.

Oxygen-propyl-succinimide.—This was prepared in the same way as the corresponding ethyl-compound, but the reaction took place more slowly. After five weeks the chloroform solution was filtered from the iodide, and it was found that a noticeable quantity of silver iodide separated on evaporating the solution, so that the residue was again taken up in chloroform and treated as described under the ethyl-ether. At the first distillation it was found that at 19 mm. pressure but a few drops came over below 153°, while almost the entire quantity boiled between 153° and 160°. On redistilling, the greater part came over at 153°–154° (pressure, 19 mm.; temperature of bath, 195°), again leaving a dark residue.

Analysis gave the following results:

	Found.	Calculated for $C_7H_{11}NO_2$.
C	59.10	59.57
H	7.95	7.80
N	10.30	9.92

The slight variation of our results from the theory would indicate the presence of a small quantity of succinimide, but as its boiling-point must be very close to that of the ether, a separation would hardly be possible, and is indeed not necessary. Like the corresponding ethyl-ether, it decomposes when boiled at ordinary pressure; gives succinimide when exposed to the air, and reacts at once with aniline. As the nitrogen-propyl-ether has a lower boiling-point than the oxygen-ether, the first portions of the distillate from the impure oxygen-ether were examined for the nitrogen-ether. It was impossible, from the boiling-points

given, that more than a small quantity of nitrogen-ether could be present, and this could hardly be separated in a pure state. So the first portions of the distillate were boiled with a strong solution of potassium hydroxide as long as any volatile base came off, the volatile part being caught in dilute hydrochloric acid. On evaporating the acid solution it was found from its insolubility in cold absolute alcohol, that the greater part of the residue consisted of ammonium chloride, but that in that portion soluble in alcohol we could positively identify propylamine by the iso-nitrile reaction. Therefore a small quantity of the nitrogen-ether is formed together with the oxygen-ether.

Nitrogen-propyl-succinimide.—For comparison we prepared this compound by the same method that Menschutkin used in making the methyl- and ethyl compounds—by distilling the acid succinate of propyl-amine. We obtained it as a colorless oil boiling at 247°–248° at 763 mm. pressure. When cooled in a freezing-mixture it solidifies and shows the melting-point 15°–16°. It boiled at 136°–137° at 27 mm. pressure. It does not form the base $C_{10}H_{10}N_2O$ with aniline. A nitrogen estimation gave N 9.92 per cent.; the theory requires 9.80 per cent.

Base $C_{10}H_{10}N_2O$.—This base is formed at once, as we have before stated, on adding aniline to one of the oxygen-ethers of succinimide. If the ether be pure the resulting base needs only to be recrystallised from alcohol. If an impure ether be used, the base can be readily purified by dissolving it in cold dilute hydrochloric acid, filtering from the dark residue and precipitating with ammonia. Its melting-point is 216°. It crystallises from hot alcohol, on cooling rapidly, in small, transparent, quadrilateral plates. Dried at 100° its analysis gave the following results:

	Found.	Calculated for $C_{10}H_{10}N_2O$.
C	69.36	68.96
H	5.79	5.74
N	16.20	16.09

The gold double-chloride of the base is precipitated from the acid solution on adding gold chloride. When prepared in the cold the double-salt forms a voluminous, sulphur-yellow precipitate consisting of microscopic needles. When the gold-chloride solution is added to the hot acid solution of the base, the double-salt separates on cooling in gold-yellow prisms. The salt should not

stand long in contact with the mother-liquor; even when filtered quickly and dried *in vacuo* over sulphuric acid, it turns green on the surface. A gold estimation gave Au = 38.46 per cent.; calculated for $C_{10}H_{10}N_2O.HCl.AuCl_3$, Au (= 196.6) = 38.38. The salt melts with decomposition at 170°.

XXXVIII.—ON SOME DERIVATIVES OF AROMATIC FORMYL COMPOUNDS.

By W. J. Comstock and R. R. Clapp.

The curiously different behavior of the sodium and silver salts of formanilide towards methyl iodide, as shown by Comstock and Kleeberg,[1] is of especial interest as the first case of a compound containing the group —NH—CO—[or—N=C(OH)—], whose sodium salt yields, under conditions which exclude dissociation, the nitrogen-ether—*i. e.* formyl-monomethyl-aniline,—while the silver salt gives the oxygen-ether—*i. e.*, methyl-iso-formanilide, $C_6H_5N{=}C{<}^{H}_{O.CH_3}$. We have continued the experiments in that direction and found that form-ortho-toluide and form-para-toluide behave in the same way: both give silver salts which, on treatment with methyl iodide, yield iso-toluides; and the sodium salt of each can be used for preparing the secondary amine. As a contribution to our knowledge of the iso-anilides, we have also prepared seven higher ethers and found that they give the same reactions,—formation of diphenyl-form-amidine by the action of aniline, by the action of a dilute acid, and by the gradual absorption of water on exposure to the air. We have also found, though without purifying and analysing the products, that methyl-iso-formanilide reacts with other primary aromatic amines as well as with aniline; and have prepared and analysed the amidines formed by treating it with hydroxyl-amine and benzyl-amine. On decomposing the silver salt of form-para-toluide in presence of dry ether with dry hydrochloric acid gas or with dry hydrogen sulphide—care being taken to have the silver salt in excess,—we found on evaporating the ether at ordinary temperature under diminished pressure, that the residue fused at 52°, as did also a specimen of pure form-para-toluide attached to the same thermometer. Nor could we observe, as the compound crystallised from ether, any

[1] This Journal **12**, 493.

difference in crystalline form which could warrant the assumption that an isomer had first been formed and afterwards transformed during the heating into the more stable ordinary form-para-toluide. This suggests the similar behavior of silver benzamide[1] towards hydrochloric acid and hydrogen sulphide; although with methyl iodide it gives the imido-ether $C_6H_5.C\begin{matrix}O.CH_3\\ \diagdown\!\!\diagup\\ NH\end{matrix}$. In the case of benzamide, however, the sodium salt could not be prepared. In form-para-toluide we have therefore a case in which sodium and silver salts regenerate the same mother-substance, while they behave differently towards methyl iodide. As we have been unable to find any experimental proof, either of the existence in the free state of an isomeric form-para-toluide, or that in treating the salts with iodides anything beyond a direct replacement of metal by alkyl occurs, the best explanation seems to be that the salts have a different structure, while only one form of the free formyl compound is capable of existing. Possibly in some of the compounds belonging to this class it will be found that both forms are capable of existing.

Derivatives of form-ortho-toluide and form-para-toluide.—The silver salts of both these compounds can be made by exactly the same method as was used in preparing silver formanilide. The preparation of the iso-form-toluides from the silver salts is exactly like the preparation of methyl-iso-formanilide, and they show the characteristic behavior of the latter compound. The two amidines were made from the iso-toluides by the action of the corresponding toluidines.

Silver form-ortho-toluide is amorphous and sensitive to light; it is insoluble in cold water.

	Found.	Calculated.
Ag	44.37	44.63

Methyl-iso-form-ortho-toluide is an aromatic oil boiling at 211°–213° at 760 mm. pressure.

	Found.	Calculated for $C_8H_{11}NO$.
C	72.42	72.48
H	7.38	7.38
N	9.71	9.39

Di-ortho-tolyl-formamidine, when recrystallised from alcohol, melted at 150°.

[1] Tafel and Enoch: Ber. d. chem. Ges. **23**, 103.

	Found.	Calculated for $C_{13}H_{14}N_2$.
C	80.30	80.36
H	7.9	7.14

This compound has already been made by Ladenburg[1] and by Senier[2] by other methods.

Silver form-para-toluide was obtained as a voluminous precipitate consisting entirely of small needles, practically insoluble in cold water; sensitive to light.

	Found.	Calculated.
Ag	44.98	44.63

Methyl-iso-form-para-toluide is an aromatic oil boiling at 216°–218° at 761 mm. pressure.

	Found.	Calculated for $C_9H_{11}NO$.
C	72.44	72.48
H	7.54	7.38
N	9.56	9.39

Di-para-tolyl-formamidine, when purified by crystallisation from pure benzene—from which it separates in flat, transparent, colorless prisms of considerable size—melts at 140°.

	Found.	Calculated for $C_{15}H_{16}N_2$.
C	80.45	80.36
H	7.21	7.14
N	12.60	12.50

This amidine was also prepared by Senier.[3]

In trying the behavior of the sodium salts of both formyl compounds towards methyl iodide, we found that the monomethyl-toluidines could be prepared either by following Hepp's method for the preparation of monomethyl-aniline, or by using sodium methylate and methyl iodide in presence of dry methyl alcohol. The yield is better when Hepp's method is followed, in which case benzene can be used in place of xylene, although the action of the sodium is then much slower. The secondary base was, however, in no case obtained absolutely pure until converted into the nitroso-compound and recovered. Monomethyl-ortho-toluidine boiled at 280°; the para-compound at 211°–212°.

Ethyl-iso-formanilide is an aromatic oil boiling at 213°–215° at 761 mm. pressure.

[1] Ber. d. chem. Ges. **10**, 1260. [2] Ibid. **18**, 2294.
[3] Loc. cit.

	Found.	Calculated for $C_9H_{11}NO$.
C	72.57	72.48
H	7.60	7.38

Propyl-iso-formanilide boils at 233°–235° at 760 mm. pressure.

	Found.	Calculated for $C_{10}H_{13}NO$.
C	73.39	73.62
H	8.24	7.98

Both of these ethers react, as before stated, exactly like the methyl-ether.

Phenyl-benzyl-formamidine.—Benzyl-amine and methyl-iso-formanilide react slowly in the cold when mixed in molecular proportions. The solid crystalline product, after being pressed free from a small quantity of oil, can be recrystallised by dissolving in strong alcohol and adding water until a permanent turbidity results. The base comes down oily at first, but gradually solidifies, forming colorless, transparent, flat prisms, melting at 80°.

	Found.	Calculated for $C_{14}H_{14}N_2$.
C	80.15	80.00
H	6.72	6.66

Action of hydroxyl-amine on methyl-iso-formanilide.—On adding methyl-iso-formanilide to an aqueous-alcoholic solution of hydroxyl-amine hydrochlorate, a white solid body separates at once. This substance dissolved in dilute alcohol gave on the addition of ammonia a precipitate consisting of small white scales which fused at 130°–131°. From the method of formation the compound is probably phenyl-methenyl-oxamidine of the structure $C_6H_5N{=}C{<}^{H}_{NH.OH}$. A combustion gave results agreeing with this formula.

	Found.	Calculated for $C_7H_8N_2O$.
C	61.71	61.76
H	6.17	5.88

Formation of di-ortho-tolyl-urea.—On distilling dry silver formortho-toluide, and recrystallising the distillate from absolute alcohol, the urea fusing at 247° was obtained.

	Found.	Calculated.
C	74.87	75.00
H	6.68	6.67

Contributions from the Sheffield Biological Laboratory of Yale University.

A STUDY OF THE PROTEIDS OF THE CORN OR MAIZE KERNEL.

By R. H. CHITTENDEN, Ph. D., *Professor of Physiological Chemistry in Yale University*, and THOMAS B. OSBORNE, Ph. D., *Chemist at the Connecticut Agricultural Experiment Station.*

(Continued from p. 468.)

Another and more successful separation of the globulin into its possible constituents was made by means of fractional heat-coagulation. Obviously, the products so obtained, or at least a portion of them, are coagulated by the process; but if the substance is composed simply of a single body, the several products or coagulums might naturally be expected to have the same composition.

In this experiment, 10 grams of globulin B were dissolved in 10-per cent. salt solution, filtered, the clear fluid heated to 50° in a roomy water-bath and a slight excess of very dilute hydrochloric acid added, by which a copious precipitate was obtained, doubtless an acid compound, leaving the fluid perfectly neutral. This precipitate was washed with salt solution, water, alcohol and ether, and weighed, air-dry, 1 gram (Preparation B^1).

The perfectly neutral filtrate, on being heated further, became turbid at 57°, with formation of flocks at 66°. The temperature, however, was raised to 70°, where it was held some time, and the precipitate finally filtered off and washed with salt solution, water, alcohol and ether. It weighed, air-dry, about 1 gram (Preparation B^2). The filtrate became turbid again at 72°, and at 75° a flocculent precipitate made its appearance, which was finally filtered off when the temperature reached 81°. This was treated like the preceding products, and when air-dry weighed 1 gram (Preparation B^3).

The clear filtrate from this latter coagulum was dialysed free from chlorides, when there resulted a separation of a globulin-like substance, which, after washing with water, alcohol and ether, weighed, air-dry, 1.43 grams (Preparation B^4).

These several products, on being dried at 110° C. until of constant weight, gave on analysis the following results:

Analysis of the HCl Precipitate at 50° (B^1).

I. 0.3539 gram substance gave 48.7 cc. N at 2.5° C. and 767.8 mm. pressure = 17.33 per cent. N.

II. 0.4731 gram substance gave 0.0016 gram ash = 0.34 per cent.

Percentage of nitrogen in ash-free substance = 17.39.

Analysis of the Coagulum at 66°–70° (B^2).

I. 0.3687 gram substance gave 47.3 cc. N at 2.5° C. and 767.8 mm. pressure = 16.15 per cent. N.

II. 0.3855 gram substance gave 0.0017 gram ash = 0.44 per cent.

Percentage of nitrogen in the ash-free substance = 16.21.

Analysis of the Coagulum at 75°–81° (B^3).

I. 0.3361 gram substance gave 44.9 cc. N at 2.5° C. and 766.1 mm. pressure = 16.78 per cent. N.

II. 0.2015 gram substance gave 0.0004 gram ash = 0.19 per cent.

Percentage of nitrogen in the ash-free substance = 16.81.

Analysis of the Globulin separated by Dialysis (B^4).

I. 0.2993 gram substance gave 0.1810 gram H_2O = 6.72 per cent. H, and 0.5674 gram CO_2 = 51.72 per cent. C.

II. 0.2595 gram substance gave 0.1596 gram H_2O = 6.83 per cent. H, and 0.4910 gram CO_2 = 51.60 per cent. C.

III. 0.3300 gram substance gave 47.9 cc. N at 2.5° C. and 762.2 mm. pressure = 18.14 per cent. N.

IV. 0.3265 gram substance gave 0.0016 gram ash = 0.49 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	51.97	51.85	..	51.91
H	6.75	6.86	..	6.81
N	..	..	18.22	18.22
S	..	..	.. }	23.06
O	..	..	.. }	
				100.00

A comparison of these results shows plainly that the globulin separable from corn meal by the process previously described, as in Preparation B, is composed of at least two dissimilar proteids, or, less probably, is broken into such bodies by the process of heat-coagulation. The products coagulable below 80° are characterised by a comparatively low percentage of nitrogen, while the product (B^4) separated by dialysis of the filtrate from the coagulum at 80° has a higher content of nitrogen than the original

globulin, resembling in this respect Preparation A^2, the more insoluble portion of globulin A^1. This relationship in chemical composition is clearly seen from the following table:

	Globulin B.	Prep. B^1.*	Prep. B^2.	Prep. B^3.	Prep. B^4.	Prep. A^2.
C	51.82	..	..	..	51.94	51.76
H	6.85	..	..	..	6.81	6.80
N	17.82	17.39	16.21	16.81	18.22	18.16
S, O	23.51	..	..	..	23.06	23.28

*In considering these results it must be remembered that Preparation B^1 is probably nothing more than an acid compound of the mixed globulins.

This close relationship in composition between the products A^2 and B^4 is strongly suggestive of their being the same body, viz., a form of phyto-vitellin especially characterised by non-coagulation below 80° and by very incomplete coagulation above that temperature, even when its solution in sodium chloride is heated to 100°.

Another point to be noted in the above experiment is, that of the 10 grams of globulin (B) started with, only 4.43 grams were recovered in the form of the products $B^1 - B^4$, just described. Naturally some loss must have occurred, especially through possible incomplete separation during dialysis of the final solution, but evaporation of the salt-free fluid from which globulin B^4 had separated revealed the presence of about 1.5 grams of non-coagulable matter, either derived from, or present in, the original globulin. The substance so obtained gave a red color with cupric sulphate and potassium hydroxide, the usual proteid reactions with Millon's reagent, no reaction with acetic acid, but a heavy precipitate with acetic acid and potassium ferrocyanide. Addition of acetic acid to a 10-per cent. salt solution of the substance gave a heavy precipitate, possibly in part of globulin, which was still further increased by saturation of the acid fluid with salt. Saturation of a neutral solution of the substance with salt gave no precipitate whatever. Nitric acid produced a distinct turbidity, and addition of an equal volume of alcohol yielded a heavy precipitate.

From this it is plainly evident that in the separation or breaking apart of the original globulin by heat-coagulation there is formed in small quantity a body, or bodies, non-coagulable by heat and readily soluble in water; in other words, bodies resembling proteoses. That such soluble substances were not present in the

original globulin was proved by boiling a small portion of globulin B in water and then filtering the hot solution. The filtrate gave no reaction whatever for proteids with the biuret test. In other words, the original globulin contained no proteose-like substances, but when dissolved in salt solution and subjected to heat-coagulation such bodies were apparently formed. This was demonstrated in several ways, among others as follows: A portion of globulin B was suspended in water, and the emulsion quickly poured into a 10-per cent. salt solution heated to 75° C. A nearly complete solution resulted, the temperature not falling below 65°. The temperature was immediately raised to 100° and the boiling continued for some minutes, thus killing any possible ferment present, after which the coagulum was filtered off. The somewhat turbid filtrate was evaporated to dryness on a water-bath, a little coagulum forming during the process, and the residue taken up in water. Addition of acetic acid to the strong salt solution produced a heavy precipitate of the vitellin-like proteid, but there still remained in solution some non-precipitable proteid, giving a distinct pink color with the biuret test. While, then, this so-called corn globulin can be approximately separated by heat-coagulation into two dissimilar globulins, there is apparently formed at the same time, presumably by hydrolysis of the less resistant globulin, a small amount of proteose-like bodies, the quantity of which appears to be dependent in part upon the duration of the heating.

The vitellin with 18 or more per cent. of nitrogen is especially characterised, as already indicated, by its pronounced insolubility in weak salt solutions, especially when cold. It is likewise more prone to separate in the spheroidal state. By making use of these facts we were able to separate it directly from the mixed globulin without recourse to coagulation. The method was as follows: 8 grams of globulin B were dissolved in 300 cc. of 5-per cent. salt solution, and the fluid filtered. The clear solution was then diluted with distilled water to about 2 litres, whereby a heavy precipitate resulted. On warming to about 45° C., however, a nearly clear solution was obtained, which on gradual cooling to 8° C. deposited at the end of 48 hours a precipitate of spheroids. This precipitate was then filtered off, dissolved in as little salt solution as possible (warmed to 50° C.), and diluted with distilled water at the same temperature, until a permanent turbidity began to make its appearance. The globulin which separated from this solution on cool-

ing, was wholly soluble in the salt fluid when warmed to 50° C. As the amount of globulin which separated by this treatment was small, the entire mixture was further diluted with an equal volume of water and the resulting precipitate collected. It was then partly dissolved in about 2 litres of quite dilute salt solution, the mixture heated to 50°, and 20-per cent. salt solution added until the globulin had entirely dissolved. On cooling this solution very slowly, ultimately near to 0°, a considerable deposit of very large spheroids resulted, which, after being washed with water, alcohol and ether, weighed, air-dry, 1.5 grams. This product (B^5), on being dried at 110° C. until of constant weight, gave by analysis the following results:

Analysis of the Globulin B^5.

I. 0.4311 gram substance gave 0.2658 gram $H_2O = 6.85$ per cent. H, and 0.8227 gram $CO_2 = 52.05$ per cent. C.

II. 0.3338 gram substance gave 49 cc. N at 3° C. and 754.2 mm. pressure = 18.10 per cent N.

III. 0.4458 gram substance gave 0.0019 gram ash = 0.42 per cent.

Percentage Composition of the Ash-free Substance.

			B^5.	B^4.	A^2.	Globulin B.
C	52.26	..	52.26	51.94	51.76	51.82
H	6.88	..	6.88	6.81	6.80	6.85
N	..	18.17	18.17	18.22	18.16	17.82
S	..	..	22.69	23.06	23.28	0.86
O	..	..				22.65
			100.00	100.00	100.00	100.00

Comparison of the analysis of this product with that of the original mixed globulin B shows that the nitrogen has been raised to correspond with the percentage in the preceding preparations of vitellin, notably B^4 and A^2, while the carbon is a trifle higher than in the latter products. Evidently, then, this simple process is sufficient to separate the vitellin from the mixed globulin; the more soluble globulin, with its lower content of nitrogen, remaining in the several solutions.

It is thus evident that the corn or maize globulin originally referred to by Weyl is a mixed substance, composed of at least two dissimilar globulins, one of which approximates in composition to phyto-myosin, the other to phyto-vitellin, although both bodies possess peculiarities of reaction not exactly in accord with the reactions of these two substances as usually described.

d. *Extraction of corn meal with water, and separation of the globulin by ammonium sulphate and dialysis.*

When corn meal is extracted with water there results a solution rich in salts, especially phosphates of the alkalies, in which more or less globulin is dissolved. Direct dialysis of such a solution is followed by separation of the dissolved globulin. It can likewise be precipitated, together with the other proteids present, by saturation of the solution with ammonium sulphate. A concentrated solution, obtained by extracting corn meal with water, when heated grows turbid at about 50° C. (the exact point depending on the concentration of the fluid), with formation of a flocculent coagulum at about 60°. At 64° the solution again becomes turbid, with formation of a second flocculent coagulum at 75°.

The globulin was separated as follows: 6.5 kilos. of corn meal were treated with 10 litres of water, with more or less stirring, for some hours, and the residue of meal re-extracted in the same manner. The united solutions, filtered clear, were saturated with ammonium sulphate. The precipitate so obtained was dissolved as far as possible in water and in 10-per cent. salt solution, leaving quite an insoluble residue. The united aqueous and salt solutions, after filtration, were dialysed until the greater portion of the salt was removed, when there resulted a decided separation of globulin. This globulin was far more insoluble in 10-per cent. solution of sodium chloride than any previous product. In other words, a much larger proportion of this originally soluble globulin passed into an insoluble modification during the process of dialysis, etc., than any product previously separated. That portion still soluble in 10-per cent. salt solution coagulated as follows: turbid at 54°–60°, with formation of flocks at 67°–71°. A second turbidity appeared in the filtered fluid at 69°–72°, but this was very slight, and was not much increased even when the solution was boiled. Addition of acetic acid, however, gave a distinct precipitate. On dialysis of the sodium-chloride solution, the dissolved globulin was deposited. It amounted to only 0.3 gram when air-dry (Preparation F). Dried at 110° C., it yielded by analysis 16.80 per cent. of nitrogen, thus agreeing approximately both in content of nitrogen and in coagulation-point with that portion of the mixed globulin B coagulable below 80°, viz., B^2 and B^3.

0.2593 gram substance gave 35.2 cc. N. at 2.5° C. and 754.9 mm. pressure = 16.80 per cent. N.

There was not enough substance for an ash determination.

A larger quantity of this globulin, sufficient for a more complete analysis, was obtained from another portion of the corn meal as follows: 5 kilos. of freshly ground corn were thoroughly extracted with water, and the filtered solution precipitated by the addition of ammonium sulphate to saturation. This precipitate was treated with water, and the globulin soluble in the dilute ammonium sulphate solution formed was, after filtration, separated from the fluid by dialysis. After washing the separated globulin with water, alcohol and ether, it weighed, air-dry, 2 grams (Preparation G^1).

Dried at 110° C. it gave on analysis the following results:

Analysis of Corn Globulin, Preparation G^1.

I. 0.1973 gram substance gave 0.1243 gram H_2O = 6.99 per cent. H, and 0.3784 gram CO_2 = 52.30 per cent. C.

II. 0.3343 gram substance gave 0.2071 gram H_2O = 6.88 per cent. H, and 0.6392 gram CO_2 = 52.14 per cent. C.

III. 0.3594 gram substance gave 50.5 cc. N at 17.1° C. and 758.5 mm. pressure = 16.57 per cent. N.

IV. 0.4590 gram substance fused with $KOH + KNO_3$ gave 0.0433 gram $BaSO_4$ = 1.28 per cent. S.

V. 0.3159 gram substance gave 0.0025 gram ash = 0.79 per cent.

Percentage Composition of the Ash-free Substance.

					Average.
C	52.71	52.56	..	..	52.64
H	7.04	6.94	..	..	6.99
N	..	..	16.70	..	16.70
S	..	..	..	1.28	1.28
O	..	..	..	..	22.39
					100.00

A duplicate of this last product was prepared from another portion of corn meal (5 kilos.) in essentially the same manner. The meal was thoroughly extracted with water, the filtered extract precipitated by saturation with ammonium sulphate, the precipitated proteids filtered off and soaked in water, by which the globulin and some other substances were dissolved. From this dilute ammonium sulphate solution the globulin was separated by dialysis of the salt, and after being washed with water, alcohol and ether, weighed, when air-dry, 2 grams (Preparation H^1).

Dried at 110° C. and analysed, it yielded the following results:

Analysis of Corn Globulin, Preparation H[1].

I. 0.2825 gram substance gave 0.1769 gram H_2O = 6.96 per cent. H, and 0.5425 gram CO_2 = 52.37 per cent. C.

II. 0.1553 gram substance gave 0.0989 gram H_2O = 7.07 per cent. H, and 0.2987 gram CO_2 = 52.45 per cent. C.

III. 0.4200 gram substance gave 59.0 cc. N at 17.2° C. and 765.1 mm. pressure = 16.71 per cent. N.

IV. 0.3118 gram substance gave 0.0021 gram ash = 0.67 per cent. (ash mainly oxide of iron).

V. 0.5500 gram substance fused with KOH + KNO_3 gave 0.0530 gram $BaSO_4$ = 1.32 per cent. S.

Percentage Composition of the Ash-free Substance.

					Average.
C	52.72	52.80	..	..	52.76
H	7.00	7.11	..	..	7.05
N	..	..	16.82	..	16.82
S	..	..	..	1.32	1.32
O	..	..	..	..	22.05
					100.00

From this description it is obvious that only a portion of the globulins contained in the corn-kernel can be withdrawn by water; in other words, the dilute salt solution which results when corn meal is extracted with water is capable of dissolving only a portion of the globulins present. More important, however, is the fact that the globulin which is so dissolved represents simply that portion of the mixed globulins, previously described, coagulating under 80°, or, to be more exact, it is apparently a body coagulating completely at 75° C. and with a content of nitrogen approximating 16.8 per cent. Furthermore, it is a globulin excessively prone to become insoluble in salt solution by long contact with water or with strong solutions of salt. In other words, it agrees closely with the general descriptions of vegetable myosin except in its peculiar coagulation-points. This view is still further substantiated by the almost complete agreement in composition with animal myosin. This relationship in chemical composition can be clearly seen from the following table:

	Corn myosin. F[1].	Corn myosin. G[1].	Corn myosin. H[1].	Coagulum at 75° from mixed globulin. B[3].	Animal myosin.*
C	..	52.64	52.72	..	52.82
H	..	6.99	7.05	..	7.11
N	16.80	16.70	16.82	16.81	16.77
S	..	1.28	1.32	..	1.27
O	..	22.39	22.05	..	21.90

*Average of the analyses of 13 different preparations of animal myosin from various sources. See Studies from Laboratory of Physiological Chemistry, Yale University, **3**, 133.

Hence, by this method of extracting corn meal directly with water, and by the use of the method of separation already described, only one globulin is obtained, with a coagulation-point of about 70° and agreeing substantially in other respects with the general properties of vegetable myosin. Doubtless the trace of a coagulum obtained at higher temperatures and on the addition of acid is due to a slight admixture of the vitellin-like body. The above statement being correct, it is obvious that the residue of corn meal remaining after complete extraction with water should yield to 10-per cent. salt solution a globulin with 18 per cent. or more of nitrogen unmixed with myosin, providing the latter body has been completely withdrawn from the tissue of the seed.

e. *Extraction of corn meal with 10-per cent. solution of sodium chloride, after previous extraction with water, and separation of the globulin by direct dialysis, and by precipitation with ammonium sulphate and dialysis.*

Extraction of corn meal with 10-per cent. salt solution, after previous extraction with water, yields a solution containing considerable globulin, which can be separated in part by addition of water and completely, or nearly so, on dialysis.

6.5 kilos. of corn meal, after thorough extraction with water (Extract F), were treated several times with an abundance of 10-per cent. salt solution, and the dissolved proteids precipitated from the filtered extract by saturation with pure ammonium sulphate. The precipitate was dissolved, so far as possible, in water and 10-per cent. salt solution, and the united fluids dialysed in running water until the bulk of the salt was removed. The globulin separated in this manner dissolved only partially in 10-per cent. salt solution. The soluble matter coagulated as follows: *slight turbidity at* 60°–63°, *with separation of a few flocks at* 71°–72°. The filtrate from this coagulum grew turbid again at 81°–82°, flocking at 91°–95°. Addition of acetic acid to this filtrate gave quite an abundant precipitate. This globulin dissolved by the 10-per cent. salt solution was again separated from the fluid by dialysis. The precipitate so obtained, when washed with water, alcohol and ether, weighed, air-dry, 4.12 grams (Preparation F^2). It was almost entirely soluble in 10-per cent. salt solution, and when subjected to heat-coagulation yielded only a slight turbidity at 63°, with separation of a few flocks at 73°. On heating this filtrate nothing further appeared other than a trifling

turbidity, even when the solution was boiled. Addition of acetic acid, however, gave a heavy precipitate. Evidently, therefore, this body is characterised especially by non-coagulation by heat, in a neutral solution, the trifling coagulum observed being unquestionably due to a trace of myosin.

Dried at 110° C. until of constant weight, and analysed, the following results were obtained:

Analysis of Corn Globulin, Preparation F².

I. 0.3781 gram substance gave 0.2295 gram H_2O = 6.74 per cent. H, and 0.7205 gram CO_2 = 51.96 per cent. C.

II. 0.3293 gram substance gave 0.2031 gram H_2O = 6.85 per cent. H, and 0.6253 gram CO_2 = 51.79 per cent. C.

III. 0.3401 gram substance gave 48.8 cc. N at 3° C. and 766.9 mm. pressure = 17.99 per cent. N.

IV. 0.3972 gram substance gave 57 cc. N at 3° C. and 756.6 mm. pressure = 17.96 per cent. N.

V. 0.7561 gram substance fused with $KOH + KNO_3$ gave 0.0337 gram $BaSO_4$ = 0.61 per cent. S.

VI. 0.8611 gram substance fused with $KOH + KNO_3$ gave 0.0446 gram $BaSO_4$ = 0.71 per cent. S.

VII. 0.3951 gram substance gave 0.0009 gram ash = 0.22 per cent.

Percentage Composition of the Ash-free Substance.

							Average.
C	52.07	51.90	..	..	..	..	51.99
H	6.75	6.86	..	..	..	..	6.81
N	..	..	18.03	18.00	..	..	18.02
S	..	..	..	..	0.61	0.71	0.66
O	..	..	..	..	..	..	22.52
							100.00

The character of this product was verified by another preparation as follows:

5 kilos. of finely ground corn, after being thoroughly extracted with water (Preparation G), were treated with an abundance of 10-per cent. salt solution, and the filtered extract directly dialysed until the salt was entirely removed. The precipitate which separated was washed with water, then redissolved in 10-per cent. salt solution, filtered from the insoluble residue, and again dialysed until the globulin had completely separated once more. This final product was very soluble in salt solutions, and weighed, after being washed with alcohol and ether, 5 grams (Preparation G^2).

A portion dried at 110° C. gave on analysis the following results:

Analysis of Corn Globulin, Preparation G².

I. 0.3063 gram substance gave 0.1857 gram H_2O = 6.73 per cent. H, and 0.5607 gram CO_2 = 49.91 per cent. C.

II. 0.3205 gram substance gave 0.1925 gram H_2O = 6.76 per cent. H, and 0.5882 gram CO_2 = 50.04 per cent. C.

III. 0.4245 gram substance gave 63.3 cc. N at 17.0° C. and 764.5 mm. pressure = 17.73 per cent. N.

IV. 0.5045 gram substance fused with KOH + KNO_3 gave 0.0355 gram $BaSO_4$ = 0.96 per cent. S.

V. 0.4490 gram substance fused with KOH + KNO_3 gave 0.0315 gram $BaSO_4$ = 0.96 per cent. S.

VI. 0.5435 gram substance gave 0.0125 gram ash = 2.30 per cent.

VII. 0.2865 gram substance gave 0.0062 gram ash = 2.16 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	51.04	51.17	..	..	..	51.10
H	6.88	6.91	..	..	..	6.90
N	..	..	18.13	..	..	18.13
S	..	..	..	0.98	0.98	0.98
O	..	..	..	..	..	22.89
						100.00

A third preparation of the same order was made as follows: 5 kilos. of corn meal, after extraction with water (Preparation H), were treated with 10-per cent. salt solution, and the filtered extract directly dialysed until the salt was removed. The separated proteid was then filtered off, dissolved again in 10-per cent. salt solution, the solution filtered, and once more dialysed until the proteid had completely separated. The globulin so obtained (Preparation H^3), after being washed with alcohol and ether, weighed 5 grams, and on analysis (dried at 110° C.) gave the following results:

Analysis of Corn Globulin, Preparation H³.

I. 0.2844 gram substance gave 0.1728 gram H_2O = 6.75 per cent. H, and 0.5196 gram CO_2 = 49.82 per cent. C.

II. 0.4564 gram substance gave 0.2699 gram H_2O = 6.57 per cent. H, and 0.8283 gram CO_2 = 49.49 per cent. C.

III. 0.3892 gram substance gave 57.4 cc. N at 16.3° C. and 759.8 mm. pressure = 17.47 per cent. N.

IV. 0.3767 gram substance gave 56.1 cc. N at 17.4° C. and 755.0 mm. pressure = 17.47 per cent. N.

V. 0.5075 gram substance gave 0.0156 gram ash = 3.07 per cent.

VI. 0.5323 gram substance gave 0.0162 gram ash = 3.04 per cent.

VII. 0.5050 gram substance fused with KOH + KNO_3 gave 0.0338 gram $BaSO_4$ = 0.92 per cent. S.

VIII. 0.5315 gram substance fused with KOH + KNO_3 gave 0.0345 gram $BaSO_4$ = 0.89 per cent. S.

Percentage Composition of the Ash-free Substance.

							Average.
C	51.38	51.04	..	..	..	..	51.21
H	6.96	6.78	..	..	..	..	6.87
N	..	..	18.02	18.02	..	..	18.02
S	..	..	..	..	0.94	0.91	0.93
O	..	..	..	..	..	..	22.97
							100.00

It is evident from these results that by this process of extraction, first with water and lastly with salt solution, a good separation of the two globulins present in the corn-kernel may be obtained; the myosin-like body passing mainly into the first or aqueous extract, the vitellin dissolving in the 10-per cent. salt solution. When we recall how difficult it many times is to separate closely related proteid bodies, the above method seems fairly successful. In the body last described we have the same globulin (vitellin) which was previously separated from the mixed globulin B, both by heat-coagulation and by what we may term recrystallisation from dilute salt solutions. In their content of nitrogen all of these preparations of vitellin show a close agreement, and, furthermore, a fairly close agreement in carbon. Moreover, the average composition of these products agrees very closely with the generally accepted composition of phyto-vitellin.

The following table shows this relationship very clearly:

	Prep. A^3.	Prep. B^4.	Prep. B^5.	Prep. F^2.	Prep. G^2.	Prep. H^2.	Phyto-vitellin.*
C	51.76	51.94	52.26	51.99	51.10	51.21	51.88
H	6.80	6.81	6.88	6.81	6.90	6.87	7.51
N	18.16	18.22	18.17	18.02	18.13	18.02	18.08
S	23.28	23.06	22.69	0.66	0.98	0.93	0.60
O				22.52	22.89	22.97	21.93

*Prepared from pumpkin seeds and analysed by Barbieri by Weyl's method (J. prakt. Chem. **18**, 102–116).

As is seen from the table of results, the vitellin is noticeably different from the corn myosin in having a smaller percentage of sulphur, the latter containing on an average 1.27 per cent. of

sulphur, while the vitellin contains only about 0.85 per cent. It is also noticeable that preparations G^2 and H^2 contain a lower percentage of carbon than the other products. What the explanation of this is we cannot say, although it is to be remembered that these two preparations of vitellin (unlike F^2) were separated from the salt solution by direct dialysis, without previous precipitation with ammonium sulphate, and possibly are not quite so pure.

As to the respective quantities of these two globulins present in the kernel, it would appear that the vitellin is greatly in excess, although it is to be remembered that the myosin is more readily changed into an insoluble modification by the process of separation, and hence considerable loss occurs.

From the foregoing it is plain that the mixed globulin first described, obtained by direct extraction of corn meal with 10 per cent. salt solution, as preparations A–D, is mainly a mixture of two globulins resembling in composition myosin and vitellin, the composition of the mixed product being readily explainable, in the main, on that hypothesis. The coagulation-points of these two globulins, however, are far from according with the coagulation-points of phyto-myosin and vitellin as usually given. What we have chosen to call corn myosin shows a tendency to coagulate at several points, as already described, but is mainly coagulable at about 70°, while the vitellin-like body in a neutral salt solution appears almost non-coagulable by heat. In fact, the latter body partakes in many respects of the character of hetero-albumose, and is perhaps as closely related to this body as to the true globulins. The myosin-like body is evidently much like the peculiar globulin (not analysed) described by Martin[1] as present in papaw juice, the coagulation-temperatures and general reactions of the two bodies being apparently much the same.

There is every indication of gradual changes being produced by the application of heat to the solutions of these globulins, and, in our opinion, the variable coagulation-points observed are an index of this fact. Sidney Martin[2] has shown that the myosin present in the kernels of wheat and rye is transformed into an insoluble body by simple warming of the 10-per cent. sodium-chloride solution of the globulin at 35°–40° C. for some hours, and Vines[3] claims that phyto-vitellin may undergo transformation into myosin. The peculiar heat-coagulation points of the two

[1] Journal of Physiology **6**, 353. [2] Ibid. **8**, "On two classes of vegetable globulins." [3] Ibid. **3**, 93–114.

corn globulins may possibly be due in part to rapid conversion into the insoluble or albuminate stage and its separation as a coagulum.

There is, however, evidence of still another globulin in the corn kernel, differing from all of the preceding preparations, but, doubtless, sometimes present in small quantity in the products already described.

f. *A more soluble globulin which separates from its solution only after long-continued dialysis.*

The two most important characteristics of a globulin are its solubility in various strengths of salt solution and its insolubility in water; hence the removal of the salt from a globulin containing solution, by dialysis, constitutes one of the most effectual methods of separating such proteids from their solutions, provided the removal of the salts is complete. Under ordinary circumstances a globulin dissolved in a salt solution separates quite rapidly when the solution is subjected to dialysis. Obviously, the rate of separation will depend greatly upon the endosmotic equivalent of the salts present and the solubility of the globulin, but under most circumstances the separation is practically complete some time before every trace of the salt is removed. Sodium chloride diffuses much more rapidly than ammonium sulphate; indeed, the latter salt requires a very long time for its complete removal, even when dialysed in running water of a fair degree of purity. The same is true of the phosphates of the alkalies present in the corn kernel, so that an extract of corn meal, for example, made with 10-per cent. salt solution, may be dialysed until every trace of chloride is removed and still give a reaction for phosphates.

In the separation of the mixed globulins from the corn kernel as already described, it will be remembered that the usual procedure was to precipitate the filtered salt extract of the meal with ammonium sulphate added to saturation. The precipitated proteids were collected on a filter, allowed to drain, and then dissolved so far as possible in water and 10-per cent. solution of sodium chloride. Obviously, such a solution after filtration when ready for dialysis, would contain, in addition to the proteids, anywhere from 5 to 8 per cent. of sodium chloride, and possibly 1 per cent. of ammonium sulphate. In separating the dissolved globulin by dialysis it was our custom to continue the dialysis until the solution failed to give any reaction for chlorides with silver nitrate and nitric acid, considering that when that point was reached the globulin would be completely precipitated. Thus, in the prepa-

ration of globulin B from 25 kilos. of corn meal, after the method just indicated, the dialysis of the sodium-chloride and ammonium-sulphate solution was continued (in running water) for two weeks, at the end of which time the chloride was entirely removed, and over 42 grams of globulin had separated. The clear filtered fluid still contained a trace of sulphate, and as an experiment it was again exposed to dialysis in small parchment bags suspended in running water, for one week longer. Greatly to our surprise, a second deposit of globulin formed, which, after being washed with water, alcohol and ether, weighed, air-dry, 2.8 grams (Preparation B^6).

The filtrate from this product was again returned to the dialysers for ten days longer, when a third deposit of globulin formed, which, after being washed and dried, weighed 1.3 grams (Preparation B^7). The filtrate from this product gave no further deposit even when dialysed in distilled water.

These two preparations were unquestionably true globulins; both were wholly insoluble in water, but dissolved readily in dilute salt solutions. Preparation B^6, dissolved in 10-per cent. solution of sodium chloride, coagulated as follows: the solution grew slightly turbid at 59° and flocked at 62°. The filtrate from this coagulum grew slightly turbid again at 69°, but there was no separation of flocks, even when the mixture was boiled, or on the addition of acetic acid. Evidently, therefore, the substance was precipitated at 62°. Addition of potassium ferrocyanide to the acid fluid, however, gave a slight precipitate, indicating that the substance was not wholly coagulable by heat, or else that some little proteose-like substance had been formed in the process.

The composition of the globulin, after drying at 110° C. until of constant weight, was as follows:

Analysis of Corn Globulin, Preparation B^6.

I. 0.3094 gram substance gave 0.1915 gram H_2O = 6.87 per cent. H, and 0.5911 gram CO_2 = 52.10 per cent. C.

II. 0.3516 gram substance gave 0.2121 gram H_2O = 6.70 per cent. H, and 0.6721 gram CO_2 = 52.13 per cent. C.

III. 0.3895 gram substance gave 47.5 cc. N at 2.5° C. and 756.0 mm. pressure = 15.12 per cent. N.

IV. 0.3798 gram substance gave 46.9 cc. N at 5° C. and 759.4 mm. pressure = 15.22 per cent. N.

V. 0.4427 gram substance fused with $KOH + KNO_3$ gave 0.0407 gram $BaSO_4$ = 1.26 per cent. S.

VI. 0.3895 gram substance gave 0.0019 gram ash = 0.50 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	52.36	52.39	..	..	..	52.38
H	6.90	6.74	..	..	..	6.82
N	..	..	15.20	15.30	..	15.25
S	..	..	..	..	1.26	1.26
O	..	..	..	..	..	24.29
						100.00

Judging from the coagulation-point and composition of this product, it is a globulin distinctly different from the preceding preparations. The above data taken together clearly prove that it is not a mere trace of myosin, vitellin, or both, which had escaped separation, although a trace of these bodies may have been mixed with it, as is indeed suggested by the turbidity at 69°, but that it represents a more soluble globulin than either of the preceding, and one containing a much lower percentage of nitrogen. It resembles myosin rather than vitellin, yet differs from them both in composition, in the temperature at which it coagulates, and in its marked solubility in very dilute solutions of salts other than chlorides.

The low content of nitrogen in this globulin is substantiated by the percentage of nitrogen in the second product (B'), which is undoubtedly the same as the preceding.

Analysis of Corn Globulin, Preparation B'.

I. 0.3051 gram substance gave 36.6 cc. N at 3.0° C. and 757.2 mm. pressure = 14.84 per cent. N.

II. 0.3987 gram substance gave 0.0085 gram ash = 2.13 per cent.

Percentage of nitrogen in the ash-free substance = 15.16.

Without doubt, traces of this globulin may be carried down with the other globulins, especially with the myosin and with the mixed globulin, and this may be the cause of the low coagulation-point occasionally observed in the other products. On the other hand, if the preliminary dialysis for the separation of the two more insoluble globulins is not continued sufficiently long, then the product obtained on subsequent dialysis will contain some myosin, and possibly vitellin.

This is well illustrated in the following experiment: The proteids precipitated from a sodium-chloride extract of 5 kilos. of corn meal (Preparation E) by ammonium sulphate, and then dissolved

in water and 10-per cent. salt solution, were dialysed in running water for one week, when a considerable separation of globulin occurred. This was filtered off, and the solution, which contained an appreciable amount of salt, was again dialysed for one week longer, yielding 1.16 grams of air-dry globulin (Preparation E^6). The filtrate, which contained a trace of sulphate, was again dialysed for one week, when there resulted a small separation of globulin, weighing, air-dry, 0.25 gram (Preparation E^7). These were dried at 110° C. and analysed with the following results:

Analysis of the Globulin E^6.

I. 0.3728 gram substance gave 48.1 cc. N at 3.0° C. and 768.3 mm. pressure = 16.20 per cent. N.

II. 0.4817 gram substance gave 0.0075 gram ash = 1.56 per cent.

Analysis of the Globulin E^7.

I. 0.1700 gram substance gave 20.6 cc. N at 3.0° C. and 767.7 mm. pressure = 15.21 per cent. N.

Not enough substance for an ash determination.

From this it is sufficiently evident that the first product (E^6) is, as might be expected, a mixture of corn myosin with the more soluble globulin; while the latter product (E^7) corresponds closely, at least in its content of nitrogen, with the preceding products of like nature.

A tabular arrangement of the analyses of what we may term pure preparations of this globulin shows a fairly close agreement in composition.

	Prep. B^8.	Prep. B^7.	Prep. E^7.
C	52.38	..	..
H	6.82	..	..
N	15.25	15.16	15.21
S	1.26	..	..
O	24.29	..	..

From the foregoing descriptions this body is to be considered as a third globulin present in small amount in the corn kernel, and characterised especially by a low content of nitrogen, 15.2 per cent., and with a coagulation-point at about 62° C.

g. Insoluble products derived from the foregoing globulins.

As is well known, many proteid bodies undergo change by long contact with water or by contact with strong salt solutions, being converted thereby into insoluble modifications resembling albumi-

nates, soluble only in dilute alkaline fluids, or, it may be, by longer action, into bodies closely resembling coagulated proteids. This is notably true of animal myosin, of freshly precipitated syntonin, and of certain vegetable globulins. We have found this likewise true of one or more of the corn globulins just described. Thus, when a perfectly clear sodium-chloride extract of corn meal is dialysed and the globulin thereby precipitated, a portion of the product is changed in the process, as evidenced by its being no longer soluble in solutions of sodium chloride of any strength. This insoluble portion, however, is dissolved by dilute solutions of sodium carbonate, being precipitated therefrom on neutralisation, apparently as alkali-albuminate. Again, in precipitating the proteids from a sodium-chloride extract of corn meal by saturation of the solution with ammonium sulphate, a portion of the globulin precipitated thereby loses its solubility in dilute salt solutions, being plainly converted into the same insoluble modification. Further, if by chance the ammonium sulphate used in the precipitation of the proteids is acid, the transformation is far more rapid and complete, apparently in proportion to the acidity. Naturally, there may likewise occur, in this case, some formation of insoluble acid compounds.

The details of the formation and separation of some of these insoluble transformation products are as follows:

1. *Insoluble products formed by the action of ammonium sulphate on the mixed globulin directly extracted from corn by 10-per cent. salt solution.*

In the preparation of the mixed globulin B, 25 kilos. of finely ground corn were extracted with an abundance of 10-per cent. salt solution at the temperature of the room, and the resultant solution filtered through filter-paper, yielding a perfectly clear fluid. All of the proteids were then precipitated by saturation of the solution at the ordinary temperature with recrystallised and perfectly neutral ammonium sulphate. This precipitate was then treated with a small volume of water, sufficient to make with the adherent salt a 1- to 3-per cent. solution of ammonium sulphate, and then with 10-per cent. solution of sodium chloride as long as the latter exerted any solvent action. As a result there remained quite an amount of insoluble matter, wholly insoluble in water and salt solutions, but readily dissolved by solutions of sodium carbonate of sufficient strength. It was, therefore, treated with a solution of

1-per cent. sodium carbonate, the fairly clear fluid filtered through paper, and the proteid reprecipitated by neutralisation with dilute hydrochloric acid. After being washed with water until free from salts, then with alcohol and ether, it weighed, air-dry, 4.7 grams (Preparation B^2). In this connection it may be well to recall the fact that in this extraction of corn there were obtained 42 grams of purified mixed globulin and 4.1 grams of the more soluble globulin, thus indicating that approximately one-tenth of the total amount of globulin was converted into this insoluble modification, presumably through the action of the ammonium sulphate. This alteration-product, after being dried at 110° C., gave on analysis the following results:

Analysis of Preparation B^2.

I. 0.4400 gram substance gave 0.2781 gram $H_2O = 7.02$ per cent. H, and 0.8657 gram $CO_2 = 53.66$ per cent. C.

II. 0.3960 gram substance gave 0.2504 gram $H_2O = 7.02$ per cent. H, and 0.7769 gram $CO_2 = 53.51$ per cent. C.

III. 0.3447 gram substance gave 44.1 cc. N at 2.0° C. and 763.2 mm. pressure = 16.02 per cent. N.

IV. 0.7012 gram substance fused with $KOH + KNO_3$ gave 0.0557 gram $BaSO_4 = 1.09$ per cent. S.

V. 0.5472 gram substance fused with $KOH + KNO_3$ gave 0.0476 gram $BaSO_4 = 1.19$ per cent. S.

VI. 0.5810 gram substance gave 0.0039 gram ash = 0.67 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	54.02	53.87	..	..	..	53.95
H	7.05	7.05	..	..	..	7.05
N	..	..	16.13	..	..	16.13
S	..	..	..	1.09	1.19	1.14
O	..	..	..	..	..	21.73
						100.00

Two similar preparations, each from 5 kilos. of corn meal, were obtained in much the same manner as the preceding, except that, through the inadvertent use of slightly acid ammonium sulphate in the precipitation of the proteids, a far larger proportion of the globulin was converted into this insoluble modification and, further, in both cases the insoluble product contained considerable matter which would not dissolve even in 1- to 3-per cent. sodium carbonate. That portion soluble in 1-per cent. sodium carbonate

was filtered off and in each case precipitated by neutralisation with dilute hydrochloric acid.

The products were then washed free from salts with water, with alcohol, and thoroughly extracted with ether (Preparations M^a and N^a).

On analysis the following results were obtained, which show fairly close agreement with the preceding data:

Analysis of Preparation M^a.

I. 0.3874 gram substance gave 0.2403 gram $H_2O = 6.89$ per cent. H, and 0.7497 gram $CO_2 = 52.77$ per cent. C.

II. 0.4460 gram substance gave 0.2749 gram $H_2O = 6.85$ per cent. H, and 0.8595 gram $CO_2 = 52.57$ per cent. C.

III. 0.4373 gram substance gave 55.5 cc. N at 7.3° C. and 765.6 mm. pressure = 15.64 per cent. N.

IV. 0.8302 gram substance fused with $KOH + KNO_3$ gave 0.0693 gram $BaSO_4 = 1.14$ per cent. S.

V. 0.6978 gram substance fused with $KOH + KNO_3$ gave 0.0577 gram $BaSO_4 = 1.13$ per cent. S.

VI. 0.9290 gram substance gave 0.0176 gram ash = 1.89 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	53.79	53.59	..	..	..	53.69
H	7.02	6.98	..	..	..	7.00
N	..	..	15.94	..	..	15.94
S	..	..	..	1.16	1.15	1.16
O	..	..	..	..	..	22.21
						100.00

Analysis of Preparation N^a.

I. 0.3777 gram substance gave 0.2315 gram $H_2O = 6.80$ per cent. H, and 0.7174 gram $CO_2 = 51.79$ per cent. C.

II. 0.3437 gram substance gave 0.2101 gram $H_2O = 6.79$ per cent. H, and 0.6502 gram $CO_2 = 51.59$ per cent. C.

III. 0.4419 gram substance gave 56.6 cc. N at 7.4° C. and 763.6 mm. pressure = 15.74 per cent. N.

IV. 0.7266 gram substance fused with $KOH + KNO_3$ gave 0.0609 gram $BaSO_4 = 1.15$ per cent. S.

V. 0.8527 gram substance fused with $KOH + KNO_3$ gave 0.0634 gram $BaSO_4 = 1.02$ per cent. S.

VI. 0.7776 gram substance gave 0.0229 gram ash = 2.94 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	53.39	53.19	..	..	..	53.29
H	7.00	6.99	..	..	..	7.00
N	..	..	16.23	..	..	16.23
S	..	..	..	1.18	1.05	1.12
O	..	..	..	..	..	22.36
						100.00

From these three analyses it is plainly manifest that these insoluble products formed in the manner indicated are essentially the same. Their composition, moreover, indicates that in the formation of these bodies a decided alteration occurs, if we assume that they are formed from the mixed globulins already described. In fact, none of the globulins thus far identified could yield products with the high content of carbon noted here without undergoing a change of considerable magnitude. Obviously, we do not know how much of this change in composition results from the action of the ammonium sulphate and how much from the action of the dilute sodium carbonate, but inasmuch as we have obtained from a mixed globulin an insoluble body having the same low content of nitrogen, without the use of the sodium carbonate, it seems fair to presume that the change in composition is independent of any action of the dilute alkaline fluid.

2. *Insoluble products formed by the action of ammonium sulphate on the globulin extracted from corn by water, and on the globulin extracted by 10-per cent. solution of salt after previous extraction of the corn with water.*

In the preparation of extract F, 6.5 kilos. of corn meal were treated with cold water—about 14 litres—in two or more portions, and the filtered solutions precipitated with neutral ammonium sulphate added to saturation. This precipitate was then treated with water and 10-per cent. salt solution as long as anything was dissolved.

The residue was then dissolved in 0.5-per cent. solution of sodium carbonate, filtered, and the proteid precipitated by neutralisation. After being washed with water, alcohol and ether, it weighed, air-dry, 1.35 grams (Preparation F*).

Analysed, it gave the following results:

Analysis of Preparation F.*

I. 0.2557 gram substance gave 0.1581 gram $H_2O = 6.86$ per cent. H, and 0.4974 gram $CO_2 = 53.05$ per cent. C.

II. 0.3350 gram substance gave 43.9 cc. N at 3° C. and 759.3 mm. pressure = 16.27 per cent. N.

III. 0.3800 gram substance gave 0.0028 gram ash = 0.73 per cent.

Percentage Composition of the Ash-free Substance.

			Average.
C	53.43	..	53.43
H	6.90	..	6.90
N	..	16.39	16.39
O	..	.. }	23.28
S	..	.. }	
			100.00

The residue of corn meal remaining after the above extraction with water, was then extracted with 10-per cent. solution of sodium chloride, the filtered solution precipitated with ammonium sulphate, and the proteids treated exactly as described under the aqueous extract. As a result, 1.45 grams of insoluble proteid were obtained, which on analysis gave the following results:

Analysis of Preparation F^{v}.

I. 0.4967 gram substance gave 0.3086 gram H_2O = 6.90 per cent. H, and 0.9537 gram CO_2 = 52.36 per cent. C.

II. 0.3520 gram substance gave 45.1 cc. N at 3° C. and 749.1 mm. pressure = 15.69 per cent. N.

III. 0.4165 gram substance gave 0.0049 gram ash = 1.17 per cent.

Percentage Composition of the Ash-free Substance.

			Average.
C	52.98	..	52.98
H	6.98	..	6.98
N	..	15.87	15.87
S	..	.. }	24.17
O	..	.. }	
			100.00

3. *Insoluble products formed through the action of water on the globulins extracted from corn meal by water and by 10-per cent. salt solution.*

The sodium chloride and ammonium sulphate solutions of the globulins filtered off from the two preceding preparations, F^{x} and F^{v}, were dialysed in running water until the salts were practically all removed and the globulins separated from their respective solutions.

On attempting to dissolve these products in 10-per cent. solution of sodium chloride, a certain proportion remained insoluble;

in other words, during the long dialysis a portion of each globulin, formerly soluble in the salt solution, had become insoluble. These insoluble products were filtered off, washed thoroughly with 10-per cent. salt solution, dissolved in 1-per cent. sodium carbonate, the solution filtered and neutralised with dilute hydrochloric acid. The precipitated proteids, after being washed with water, alcohol and ether, weighed, air-dry, respectively 1.2 grams (Preparation F^{za}) and 1.73 grams (Preparation F^{ya}), the former having come from the globulin extracted by water alone, and hence presumably formed from the myosin-like globulin, while the latter product, F^{ya}, on similar grounds must have been formed from the vitellin-like globulin or from some adherent body.

These two products, on analysis, gave the following results:

Analysis of Preparation F^{za}.

I. 0.2278 gram substance gave 29.8 cc. N at 2.5° C. and 756.9 mm. pressure = 16.24 per cent. N.

II. 0.3678 gram substance gave 0.0029 gram ash = 0.79 per cent.

Percentage of N in the ash-free substance = 16.37.

Analysis of Preparation F^{ya}.

I. 0.2795 gram substance gave 0.1740 gram H_2O = 6.92 per cent. H, and 0.5302 gram CO_2 = 51.74 per cent. C.

II. 0.2844 gram substance gave 38.3 cc. N at 3.0° C. and 760.3 mm. pressure = 16.74 per cent. N.

III. 0.4025 gram substance gave 0.0018 gram ash = 0.45 per cent.

Percentage Composition of the Ash-free Substance.

			Average.
C	51.97	..	51.97
H	6.95	..	6.95
N	..	16.82	16.82
S	..	..	24.26
O	..	..	
			100.00

Arranging these several results in tabular form, it becomes easy to draw certain general conclusions from the data:

	B^z.	M^z.	N^z.	F^z.	F^y.	F^{za}.	F^{ya}.
C	53.95	53.69	53.29	53.43	52.98	..	51.97
H	7.05	7.00	7.00	6.90	6.98	..	6.95
N	16.13	15.94	16.23	16.39	15.87	16.37	16.82
S	1.14	1.16	1.12	23.28	24.17	..	24.26
O	21.73	22.21	22.36				

	Myosin-like globulin.	Very soluble globulin, B^{g}.	Vitellin-like globulin, F^{g}.
C	52.72	52.38	51.99
H	7.05	6.82	6.81
N	16.82	15.25	18.02
S	1.32	1.26	0.66
O	22.05	24.29	22.52

With the exception of the product F^{vii}, all of these insoluble bodies have the same general composition, and are alike characterised by a high content of carbon. Taking into consideration the percentage of nitrogen in these bodies and the nitrogen of the several globulins present in the corn kernel, it is evident that the vitellin-like globulin cannot well be considered as an antecedent of these insoluble products. These latter bodies are unquestionably formed from the myosin-like globulin and the still more soluble globulin with 15.25 per cent. of nitrogen. Doubtless it is this greater tendency of these two globulins to pass into insoluble modifications which facilitates the purification of the vitellin-like globulin. Thus the like preparations, F^{x} and F^{v}, coming as they do from the aqueous extract and from the sodium-chloride extract of the corn respectively, indicate a common origin, and it can be explained only on the supposition (certainly plausible enough) that the myosin-like globulin, not being wholly dissolved by the water extract, is dissolved together with the vitellin by the 10-per cent. salt solution and then later changed into the insoluble modification just described. Again, the content of sulphur is of significance in this connection, in that the myosin-like globulin and its still more soluble neighbor are both characterised by a fairly high content of sulphur, while the vitellin-like globulin contains less than 1 per cent. of this element.

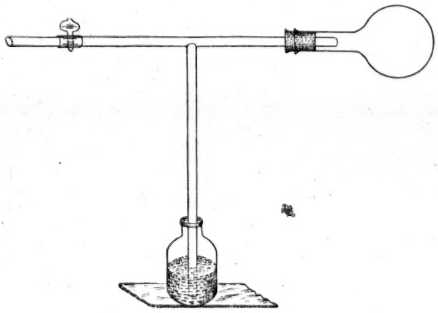
In conclusion, then, we are apparently justified in making the statement that through the long-continued action of water and strong solutions of salt, as ammonium sulphate, the two globulins with a low content of nitrogen are gradually changed into insoluble modifications, which are especially characterised by a relatively high content of carbon.

(*To be continued.*)

A SIMPLE FORM OF APPARATUS FOR A COMMON LECTURE EXPERIMENT.

By W. A. Noyes.

The apparatus usually employed to demonstrate that the volume of sulphur dioxide formed by burning sulphur equals the volume of oxygen consumed, is expensive and somewhat difficult to manage. I have found that the simple arrangement illustrated below answers excellently for the purpose.



In the flask, having a capacity of 250 to 300 cc., is placed a small piece of sulphur. The flask is then filled with oxygen by displacement of the air. The rubber stopper on the end of the T-tube is then inserted, and by means of the water air-pump the flask is exhausted till the mercury rises to a height of about 300 mm. in the lower arm of the tube. After closing the stop-cock and placing a mark at the top of the mercury in the tube, the sulphur is ignited by heating the flask with a small flame. The combustion takes place quietly, and when it is completed, the flask, being thin, cools quickly to its original temperature. When cold the mercury will stand very nearly at the same level as before the combustion, usually a very little higher.

Rose Polytechnic Institute, *October*, 1891.

THE REACTION BETWEEN TRI-PHENYL-METHANE AND CHLOROFORM IN THE PRESENCE OF ALUMINIUM CHLORIDE.

By C. E. Linebarger.

Messrs. Friedel and Crafts,[1] in investigating the reaction of chloroform on benzene in the presence of aluminium chloride, found that phenyl-anthracene was formed as a secondary product. The most probable explanation of its formation is that the chloroform reacts upon the tri-phenyl-methane formed in accordance with the equation:

$$(C_6H_5)_3CH + CHCl_3 = C_6H_4\begin{<}{C \atop C}\end{>}C_6H_4 + 3HCl.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H \atop C_6H_5$$

On the suggestion of M. Friedel, I took up the investigation of the subject, and have found that chloroform really does act upon tri-phenyl-methane in the presence of aluminium chloride, giving as principal product phenyl-anthracene. After numerous experiments, I found that the following way of conducting the reaction gave the best yield. In no case, however, was a very good yield obtained; the best being about 15 per cent. of the theoretical. Also the amount of phenyl-anthracene obtained was not at all uniform, experiments carried out under perfectly similar conditions giving quite different results.

To a solution of 50 grams pure tri-phenyl-methane in 600 grams anhydrous chloroform, 40 grams of aluminium chloride were added in three portions. On the addition of the first portion hydrochloric acid began to pass off slowly, more rapidly on heating to 40°–50°. When all the aluminium chloride had been added, I heated to gentle boiling for a few minutes. I found it not advisable to boil longer than was necessary to cause a little less than the theoretical quantity (calculated according to above equation) to pass off. The contents of the flask were now treated first with cold, then with boiling water. The chloroform solution when drawn off was distilled and the residue dissolved in a little benzene. On adding a relatively large quantity of petroleum ether, a resinous precipitate was thrown down, which was filtered off. I

[1] Ann. chim. phys. (6) 1, 495.

distilled off the mixture of benzene and petroleum from the filtrate and crystallised the residue from alcohol. By two crystallisations almost white tablets of phenyl-anthracene were obtained.

In regard to the properties of the phenyl-anthracene obtained in this way, I found them to agree entirely with those found by other investigators. A melting-point determination carefully made with a good thermometer divided in tenths of a degree, gave 152.8°.

An analysis gave

	Calculated for $C_{20}H_{14}$.	Found.
C	94.48	94.57
H	5.52	5.49

From the alcoholic mother-liquors I succeeded in isolating a substance crystallising well, and melting at 87°–88°. v. Baeyer[1] mentions, as one of the products of reduction of phenyl-oxanthranol, a substance melting at 86°–88°, which he takes to be a mixture of di- and tetra-hydrides of phenyl-anthracene. I did not obtain enough of the substance in question to make an exhaustive study, it being formed in minute quantities only; but from the analysis I conclude that it is a hydride of phenyl-anthracene. The results of the analysis would seem to show that it was the di-hydride, and it would be possible for a reduction to take place in the reaction. Nevertheless it is difficult to conceive how the reduction could give the tetra-hydride.

The analyses gave

	Calculated for $C_{20}H_{16}$.	Calculated for $C_{20}H_{18}$.	Found. I.	Found. II.
C	93.78	93.03	93.64	93.7
H	6.22	6.97	6.35	6.49

The formation of phenyl-anthracene by the action of tri-phenyl-methane upon chloroform in the presence of aluminium chloride, throws some light upon the mechanism of the reaction between benzene and chloroform in the presence of aluminium chloride. At a certain stage of the reaction the chloroform begins to act upon the newly formed tri-phenyl-methane to form phenyl-anthracene and other products. Thus a certain portion of tri-phenyl-methane is destroyed and the yield is less. On this score an objection might be raised against the methods in which the reaction is prolonged for a long time. It is true, hydrochloric acid passes off all the time, but it is not entirely due to the

[1] Ann. Chem. (Liebig) **202**, 62.

action of chloroform on benzene. The tri-phenyl-methane is also acted upon by the chloroform. What renders this more plausible is, that in the method of Friedel and Crafts, where the reaction is only continued for a few hours, a better yield is obtained than by any other method.

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THE ACTION OF BENZENE ON BENZAL CHLORIDE IN THE PRESENCE OF ALUMINIUM CHLORIDE.

BY C. E. LINEBARGER.

Nearly all the text-books on organic chemistry state that tri-phenyl-methane is formed by the action of benzal chloride on benzene in the presence of aluminium chloride, in accordance with the equation:

$$C_6H_5CHCl_2 + 2C_6H_6 = (C_6H_5)_3CH + 2HCl.$$

The only recorded experimental proof of this assertion, as far as my knowledge goes, is in a foot-note by Böttinger,[1] who remarks that small quantities of tri-phenyl-methane are formed if benzal chloride and benzene be warmed together with a little zinc dust. I have made a more detailed examination of this reaction, in the hope of obtaining, not only tri-phenyl-methane, but also a dihydride of di-phenyl-anthracene. That a dihydride of di-phenyl-anthracene would be formed in a reaction of this kind seemed probable, as Anschütz,[2] by the reaction of ethylidene bromide on benzene in presence of aluminium chloride, obtained the dihydride of di-methyl-anthracene.

It appeared to make no difference in the yield whether the benzal chloride was run into the benzene containing the chloride of aluminium, or the aluminium chloride added to the mixture of benzene and benzal chloride.

One noteworthy feature of the reaction was the small amount of aluminium chloride required. After several trials with different proportions of the ingredients, I decided upon the following method of conducting the reaction: I added 25 grams aluminium

[1] Ber. d. chem. Ges. **12**, 976. [2] Ann. Chem. (Liebig) **235**, 305.

chloride to a mixture of 200 grams benzal chloride (b. p. 206°–207°) and 1000 grams benzene, and gently heated on the water-bath. At about 40°–50° the reaction begins, and at 50°–60° takes place quite rapidly. When nearly the theoretical quantity of hydrochloric acid has passed off, which occurs in about two hours, the contents of the flask are heated to boiling for a few minutes. When cool, the product of the reaction is treated with water. After drawing off the water from the benzene solution, I distilled off the latter and subjected the residue to fractional distillation.

Almost nothing passed over below 260°; at this point a decomposition of higher-chlorinated products took place with evolution of acid fumes. Between 300°–360° the larger portions passed over and the distillate solidified in the receiver. Another small distillate was collected between 360°–420°, and also one between 420° and red heat.

The fraction between 300°–360° dissolved readily in hot benzene, from which on cooling the characteristic crystals of the compound of benzene and tri-phenyl-methane were deposited. By crystallisation from alcohol, pure tri-phenyl-methane was obtained. With 200 grams benzal chloride I obtained on an average about 80–90 grams pure tri-phenyl-methane, or about 30 per cent. of the theoretical yield. If the benzal chloride be pure, but traces of di-phenyl-methane are formed. The method is certainly excellent for obtaining tri-phenyl-methane as regards cheapness, rapidity of execution and yield.

The properties of tri-phenyl-methane, prepared by this reaction, are exactly those described by other investigators. I made determinations of both melting- and boiling-point. The melting-point, taken with a corrected thermometer divided in tenths of a degree, was 93.4°. The boiling-point, taken with a Baudin corrected thermometer, was 357° under 758 mm.

From the higher-boiling distillates I obtained a hydrocarbon with the composition $C_{26}H_{20}$, which is without doubt the dihydride of di-phenyl-anthracene.

Dihydride of di-phenyl-anthracene, $C_6H_4<\begin{matrix}H\ C_6H_5\\ C\\ C\\ H\ C_6H_5\end{matrix}>C_6H_4$.—The distillates boiling above 400° were redistilled under a pressure of

about 25 mm. At 200° a light-yellow liquid passed over which solidified in the receiver; this proved to be tri-phenyl-methane. At 250° I changed the receiver and collected a small distillate between 250°–300°. I now removed the thermometer, changed the receiver, and heated as long as anything distilled. The dark-red viscous distillate thus obtained was dissolved in a hot mixture of alcohol and benzene. After standing some time, a dark-red oil separated out. The clear solution was decanted from this oil, and it gave by slow evaporation a crop of microscopic crystals. By two crystallisations from boiling benzene, these were obtained perfectly pure and white. The results of an analysis were:

	Calculated for $C_{28}H_{20}$.	Found.
C	93.97	93.82
H	6.03	6.3

The dihydride of di-phenyl-anthracene forms a white crystalline powder when crystallised from hot benzene, in which it is not very soluble. The crystals under the microscope are seen to be rhombic prisms. Its melting-point is 164.2°; its boiling-point 437°. It is insoluble in water, soluble in alcohol, ether, toluene and xylene.

Bromine in chloroformic solution does not act upon it in the cold. At the boiling-point of the chloroform, however, hydrobromic acid is given off, and by continuing the heating two hydrogen atoms may be replaced by bromine.

Di-phenyl-anthracene bromide, $C_6H_4<\begin{matrix}Br\ C_6H_5\\ C\\ C\\ Br\ C_6H_5\end{matrix}>C_6H_4$.—Four grams bromine were added to five grams dihydride of di-phenyl-anthracene dissolved in 200 cc. chloroform, and the chloroform kept vigorously boiling with reflux-condenser until hydrobromic acid ceased to pass off. The chloroform was now distilled off and the residue crystallised from alcohol. With one or two crystallisations it was possible to obtain a pure product.

An analysis gave:

	Calculated for $C_{28}H_{16}Br_2$.	Found.
Br	32.65	32.47

Di-phenyl-anthracene bromide melts at 127° with slight decomposition. It crystallises from alcohol in small tablets. It is soluble in alcohol, benzene, chloroform and toluene.

The yield of dihydride of di-phenyl-anthracene is very small. From about 2000 grams of benzal chloride employed in the experiments only about 20 grams of dihydride of di-phenyl-anthracene were obtained.

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SOLID FORMULÆ; MODELS FOR USE IN TEACHING ORGANIC CHEMISTRY.

BY ARNOLD EILOART.

In lecturing on stereochemistry I have found models similar to those here described very helpful, and believe that they will prove useful also in general lectures on organic chemistry, elementary as well as advanced. These models do not pretend to represent any new conception as to the space-relations of atoms, but merely conveniently to represent established conceptions; further, they are not intended to supersede existing models, but to supplement them, for if only one sort of model be used there is danger that what is accessory may be considered essential; but when the same idea is represented by a variety of models it is seen that the essential is common to all, while variation of the accessories makes plain their non-essential nature.

That which is common to all models representing the space-relations of radicals attached to a carbon-atom is the prominence of four equidistant points; for although different radicals probably place themselves at different distances from the central carbon, they are for convenience represented as equidistant from it and from one another. Thus Van't Hoff used a regular tetrahedron, of which the centre and the four corners represented the relative positions of a carbon-atom and the radicals attached to it, a carbon-atom attached to unlike radicals being represented by a tetrahedron with the corners of different colors. The essence of the present device is the use of letters instead of colors at the corners

of the tetrahedra. As by means of caps fitting over the tetrahedron corners Van't Hoff could change their colors, so can the letter-symbols be changed by exchanging one cap for another. In addition, means are provided for supporting the tetrahedra so that the caps may be readily changed, for holding the cap on the corner it covers, for connecting the tetrahedra by one or by two corners, and for easy transition from the single to the double connection as well as *vice versa*.

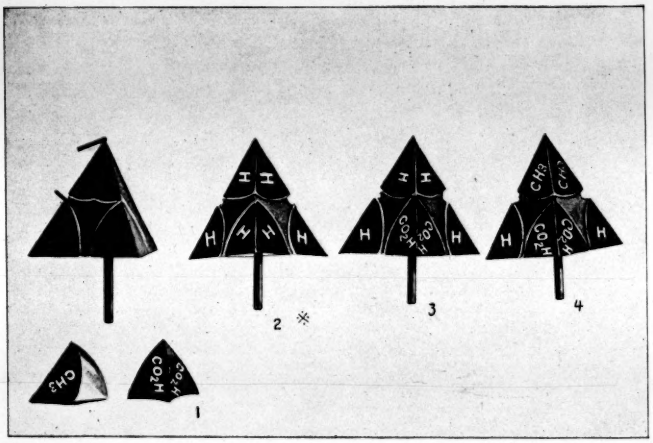
The figures (see Plates) show the arrangements.[1] It will be seen that when the tetrahedra are joined at one corner only the hinged connecting rod remains straight, because it sinks just so far into the lower tetrahedron that the hinge is covered. To convert the corner-connection (single-bond) into the edge-connection (double-bond), a pin is placed in the middle of that edge of the lower tetrahedron which is to be joined to the upper one, the latter is slightly raised, the little finger of the hand which raises it is used to lift the hinged rod till the hinge is free, and now any free corner of the upper may be made to touch the proper corner of the lower tetrahedron, and the pin will make the connection secure. This pin fits into the lower tetrahedron so tightly that it remains there when the edges are separated for restoration of the single-bond. These manipulations take a few seconds only. To test the durability of the arrangement by which the caps are held in place, some of them have been put on and off many times, one of them 300 times; all those tested work as well as when first used. To put a cap on and off takes less than a second.

The Use of the Models for illustrating General Organic Chemistry.

It is true that in using the models for this purpose our instructions are liable to become permeated with ideas as to the relative positions of atoms, ideas which we have not hitherto allowed to exert much influence on such teaching. But it is also doubtless true that an analogous statement could at one time have been made with regard to the introduction of structural formulæ. These, however, have long since emerged from the study of the investigator who, to make plain to himself his own conceptions, first used them, and now cover our blackboards. Similarly stereochemical models which already find a place on the study-

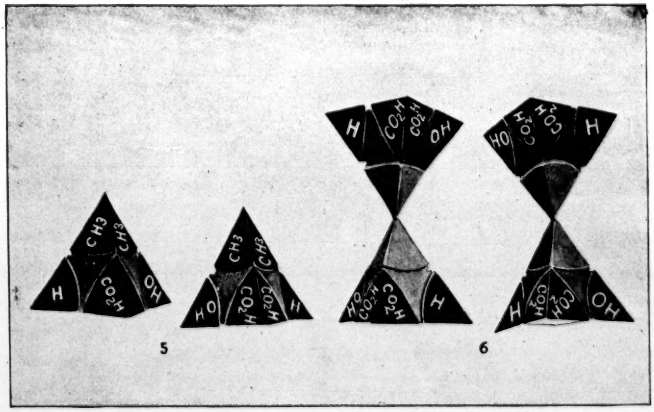
[1] The upright rods on which the models are supported have been omitted from the plates.

PLATE I.



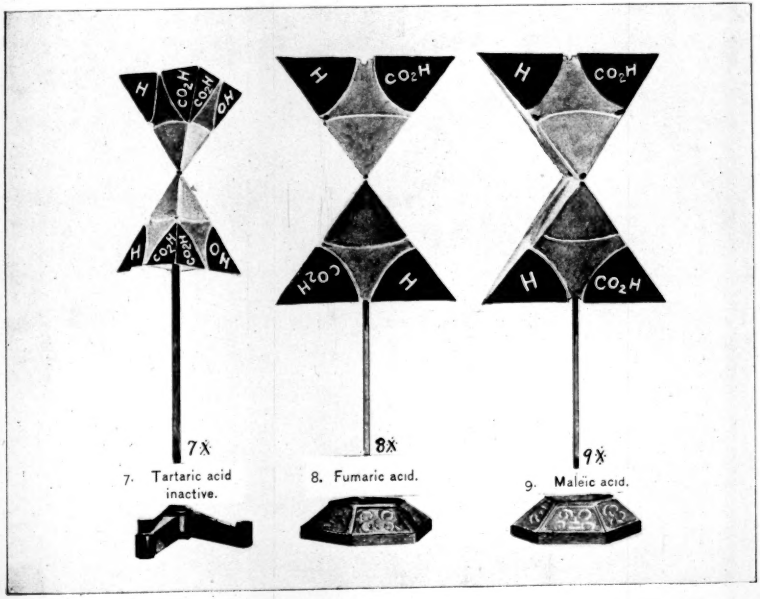
1. Separate parts of model. 2. Methane. 3. Acetic acid. 4. Propionic acid.

PLATE II.



5. Lactic acids (right and left-handed). 6. Tartaric acids (right and left-handed).

PLATE III.



7. Tartaric acid inactive.

8. Fumaric acid.

9. Maleïc acid.

tables of the few, must sooner or later cover our lecture-tables. Solid formulæ will partially supersede structural formulæ, as these have partially superseded empirical formulæ, and the gain in our power of concise and rapid thinking, similar in origin, will possibly be comparable in degree. As structural formulæ are more cumbersome to use than empirical, so are solid more cumbersome than structural formulæ; but in each case the more ample formula best stenographs our thought. And when a solid formula is once arranged it takes no more time to alter it, by exchanging one cap for another, than to turn to the blackboard and make the alteration in a written formula; in manipulating the models we have, too, the advantage of always facing the audience.

As to the dangers which are incident to the use of all formulæ, the history of stereochemistry shows that we must especially guard against proceeding faster than our knowledge warrants in the allotment of formulæ; on the other hand, the danger of cramping rather than stimulating thought is perhaps less formidable in the case of solid than of other formulæ.

It is well, however, in discussing the advantage of using solid formulæ, to consider particular cases. For instance, the fact that it is matter of indifference which hydrogen-atom in methane be exchanged for a given radical has been illustrated by means of the models of Kekulé;[1] the solid formulæ are equally effective, and with them we may illustrate the replacement of hydrogen by any given radical, and this without straining the memory to connect H, Br, CH_3, etc., with the particular color assigned to it. Next, the cap marked CH_3, which has represented methyl acting as an element, may be replaced by a block with three caps marked H; with the aid of this double means of representation the conception of a compound radical is readily imparted; similarly we may develop $-C_2H_5$ to $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}H$, or to $-\overset{H}{\underset{H}{C}}-CH_3$. The derivation of the series CH_4, C_2H_6, etc., and of the general formula C_nH_{2n+2} is clearly seen; the tendency to ring-formation and the stability of rings of five or six carbon-atoms are explained at once.[2] Further, we may show the double- and the triple-linking of carbon-atoms; the diminution in the number of atoms bound by carbon-atoms so linked is represented by the impossi-

[1] See, however, Le Bel: Bull. Soc. Chim. [3] **3**, 788.

[2] See Plate in the report on Stereochemistry.

bility of covering by caps those of the tetrahedron corners which are in contact, and the formulæ C_nH_{2n} and C_nH_{2n-2} are deduced. Some of the facts mentioned might be represented by plane structural formulæ; but the representation of all the facts in the same way strengthens their connection in the mind.

The Special Use of the Models in Stereochemistry.

For a general explanation of the isomerism of compounds of the type $CR^1R^2R^3R^4$, the models of Kekulé or those of Van't Hoff may be used; it is when we have to deal with particular compounds (such, for instance, as the lactic acids) that we find the use of the models with letter-symbols desirable if not indispensable.

We may also not only show the general relations of radicals attached to two carbons singly-linked, the effect of the relative rotation of these carbons and of the inclination of the axes round which the two sets of radicals are ranged, but we may give solid formulæ to any compound of the type $C_2R^1R^2R^3R^4R^5R^6$; we may show, side by side, the three solid formulæ for tartaric acid, how two of these together represent racemic acid, and how this acid is necessarily the product of the addition of four hydroxyl groups to two molecules of fumaric acid, while it is mesotartaric acid that must result from similar treatment of maleïc acid. The solid formulæ of fumaric and maleïc acid render Van't Hoff's theory as to their isomerism at once clear, and all the transformations attributable to their different configuration are traced with ease by means of the models. There are, in fact, but few configurations known to the stereochemistry of carbon which cannot be thus represented.

An objection to the particular form of model here described is yet to be noticed. The configurations of Wunderlich perhaps more nearly represent the truth than do those of Van't Hoff, and the former, it may be urged, should be taken into account in any attempt to extend the use of stereochemical models. Unfortunately, Wunderlich's configurations would require the use of transparent models in order that the formulæ of the radicals attached to the carbon-atoms might all be visible at once. Besides, the models described may be used to illustrate the general nature of the theories of Wunderlich, and they represent after all the four points equidistant in space about which Wun-

derlich's figures for the form of the carbon-atom are described. To illustrate further the theories of Wunderlich and Skraup[1] two large round-bottomed flasks may be used. The necks serve as handles, and four equidistant points on the outside of each flask are marked with colors or letters.

Details of Construction.

The dimensions given need not be followed exactly; but for every model the dimensions should be the same, so that the parts may be interchangeable.

The *tetrahedra*, 13 cm. (5 in.) in the edge, are cut from a long triangular prism of white wood 13 cm. in the side. At each corner is bored a hole of 0.5 cm. ($\frac{5}{16}$ in.) in diameter and 4 cm. ($1\frac{5}{8}$ in.) deep. Lining this and firmly fitted into it is a brass tube of 0.4 cm. ($\frac{5}{32}$ in.) internal diameter, projecting only about 0.1 cm. Slight variation in the length projecting, in order to correct inequality in the length of the edges, is permissible. In the middle of each edge is bored a hole 0.5 cm. wide at the mouth and tapering to 0.3 cm. ($\frac{1}{8}$ in.) at 0.3 cm. from the mouth; the hole then continues 3 cm. ($1\frac{1}{4}$ in.) deeper, the diameter of this part being adjusted to that of the rod which is to support the block. (A bill-file with loaded foot may be used.) In the middle of one face is bored a similar hole to fit the rod; no enlargement at mouth. If many connected blocks are to be supported it is well to make in the middle of one face a hole large enough to receive the rod of a retort-stand having three feet.

The position of the grooves on the tetrahedron-faces is marked by drawing a line along the free edges of a cap pushed home on one of the tetrahedron-corners. The groove, which at its widest part is about 0.3 cm. across, slopes downwards towards the curve so described, where its depth is greatest—not more than 0.08 cm. ($\frac{1}{32}$ in.) Six blocks suffice for most purposes, but for benzene-derivatives more will be necessary.

The *caps* are made of tin-plate about 0.5 mm. ($\frac{1}{50}$ in.) thick, and measure about 6.3 cm. ($2\frac{1}{2}$ in.) in the edge; fitted on to a block, a cap then comes within about 0.5 cm. ($\frac{1}{4}$ in.) of the centre of the block-edge. The cap is painted black, and on each of its three sides the symbol of the element or group for which it stands is

[1] Monatsh. Chem. **12**, 146.

stencilled in white or gold.[1] It is well to have about forty caps, six marked H, four Cl, four Br, four I, four OH, two CH_3, two C_2H_5, two C_6H_5, four COOH, and some caps unlettered for marking with chalk at will.

The *hinged rods* have each limb 3.5 cm. ($1\frac{7}{16}$ in.) long, and are 0.3 cm. ($\frac{1}{8}$ in.) thick, so that they slide freely in the brass tubes of the corner holes.

The *pins* are 2.5 cm. (1 in.) long, 0.5 cm. ($\frac{3}{16}$ in.) thick in the middle, and taper down to 0.3 cm. at the ends. A pin pushed into one of the holes in the edge-centres must sink in a little more than half way; the part left outside the hole will then not fit a similar hole too tightly, so that another block may be put on and removed without disturbing the pin; that this may be done without allowing too much side-play to the blocks joined by the pin, care in adjusting the dimensions of the pins and holes is necessary.

The dimensions given are those of the models used by me; for a very large lecture-room larger blocks and caps would be necessary in order that the letters might be written larger; but blocks 15 cm. (6 in.) and caps 7.5 cm. in the edge would answer every purpose.

The work connected with this paper was done at Cornell University. I take this opportunity of expressing my thanks to Mr. Lester J. Young, instructor in Architecture, without whose valuable aid in word and deed it would have been hardly possible to bring the models to their present state.

NEW YORK, *October*, 1891.

THE EFFECT OF NASCENT HYDROGEN AND NASCENT OXYGEN ON NITRIC ACID.

BY WM. F. HALL.

In the periodic classification of the elements nitrogen is immediately connected with phosphorus, and rightly so, for there are many analogies between them. At the same time a most serious variance is found in their behavior toward oxygen. Phosphorus

[1] To protect the letters two small knobs of solder are placed on each face, one near each end of its free edge. The caps may then be packed one inside another without injury. This addition had not been made when the photographs were taken.

readily combines with this element to form oxides which, uniting directly with water, produce stable acids; whereas nitrogen combines with oxygen only when aided by a third substance or under extraordinary conditions, and the oxides form but one acid in any way stable. So great, indeed, is the difference in this respect that the question is legitimate whether nitrogen is in its proper place; and if it were shown that nitrogen could not form acids corresponding to those of phosphorus, it would not be unreasonable to refuse it its present position in the natural scheme.

The probability, however, is that nitrogen can form as many oxygen-acids as phosphorus, for every day, bringing announcements of new compounds, encourages the expectation that the nitrogen-acids in question will in due time be produced. Indeed, the most interesting bodies of recent discovery are two nitrogen hydrides, hydrazine and azoimid, or hydrazoic acid, having the formulæ N_2H_4 and HN_3 respectively.

The only stable acid of nitrogen at present known is nitric acid, HNO_3, which differs from the acid corresponding to the stable orthophosphoric acid, H_3PO_4, by a molecule of water. In solution then, so far as we know, a corresponding nitrogen-acid can exist, formed according to the reaction

$$HNO_3 + H_2O = H_3NO_4.$$

Although all attempts at its isolation have failed, an examination by the freezing-method of Raoult would probably throw some light on the subject. This acid would be ortho-nitric acid, while the ordinary nitric acid would become the meta-acid. Similarly we should expect to have ortho-nitrous acid, H_3NO_3, which indeed we may expect to obtain by the addition of hydrogen to nitric acid, thus

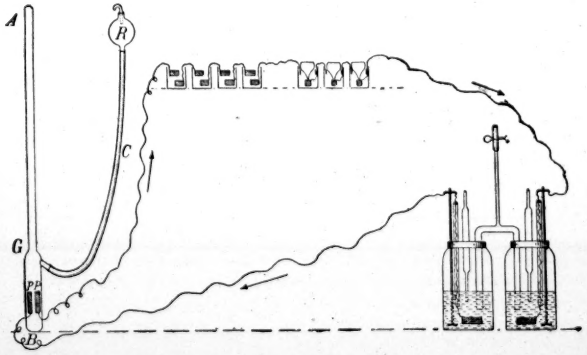
$$HNO_3 + 2H = H_2NO_3;$$

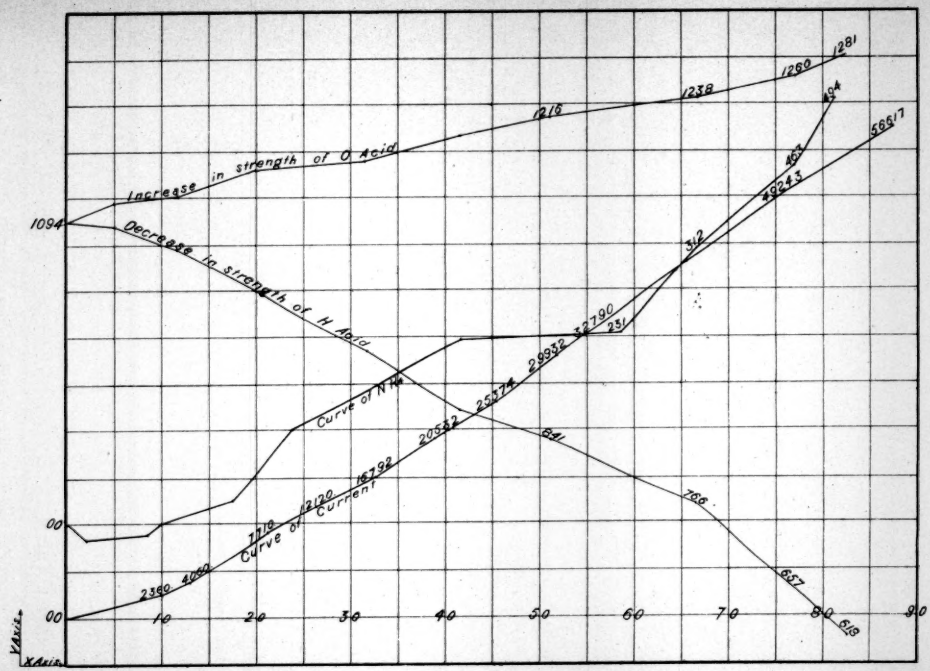
and doubtless, further, producing ammonia and the ammonium salt of hydrazoic acid. Wherefore a study of the action of nascent hydrogen upon nitric acid must throw light upon these compounds.

The following is an account of preliminary experiments to determine the conditions of action of nascent hydrogen on nitric acid. The results are principally negative, but nevertheless seem to be worth publishing, as at the end of the investigation, which had to be abruptly terminated at the close of the session, some interesting results were indicated. At the same time the action of nascent oxygen on nitric acid was observed.

Decomposition by means of electricity presented the most favorable way of simultaneously obtaining the nascent gases. The apparatus and arrangement was as follows: The two glass jars containing the electrolyte were each about 7 in. high by 4 in. in diameter, connection between them being made by a tube, $\frac{1}{2}$ in. in diameter, bent thus ⌒, the upright arm being a tube of much smaller bore, closed by rubber tubing and a pinch-cock, so that by releasing the pinch-cock the liquid in the connecting-tube would fall, thus breaking connection. Through the cork closing each jar extended the conducting-wire, protected from the acid by glass tubing; a 5-cc. pipette and a glass stirrer, the lower end of which was curved into a spiral so that the liquid might be thoroughly agitated. The platinum electrodes, not covered with platinum black, were $1\frac{5}{16} \times \frac{5}{16}$ in. After carefully cleaning and somewhat roughening the surfaces in order that the gas might freely escape, they were placed with the flat sides vertical.

The decomposing current was 303 milli-ampères per square centimeter of surface of the electrode, with an electromotive force of about 7.5 volts. Three Meidinger flask-cells were at first tried in series, the connecting-tube being then only $\frac{8}{16}$ in. in diameter; the current was not sufficiently strong until the number of the cells had been increased to seven and the connecting-tube exchanged for one of $\frac{8}{16}$-in. diameter. The accompanying sketch will show the arrangement of the apparatus.




Increase in strength of O Acid
Decrease in strength of H Acid
Curve of NH3
Curve of Current
1094
1216
1238
1260
1281
494
466
432.5
312
231
32790
29932
25574
20532
16792
12100
7718
4060
2360
641
786
657
618
566.7
00
00
10
20
30
40
50
60
70
80
90
Y Axis
X Axis

To measure the current a gas-voltameter was chosen because of its convenience. The tube was carefully calibrated with mercury, and a table of the graduations so arranged that a reading of the level of the liquid gave directly the current that had flowed since filling the tube.

In the sketch, *AB* is the tube, graduated from *A* to *G*. The gas-exit was placed some distance above the electrodes and, the bore of the lower portion of the tube being quite large, the electrodes were never exposed. These electrodes were $2 \times \frac{5}{16}$ in. The voltameter was so clamped in an upright position that it might be partially inverted, thus allowing the gas to escape and the tube to be refilled from the reservoir *R*, through the rubber tube *C*.

According to Mascart (see Stewart and Gee), the use of phosphoric acid (H_3PO_4) in a voltameter will prevent the formation of ozone; for that reason phosphoric acid, diluted with water, 3 to 10, was used. Before using the voltameter, gas was passed through the liquid for several days, to saturate it. The tube allowing the gas to escape from the reservoir *R* was very small and bent downward to retain some of the electrolytic gas and keep the liquid covered with it.

Into each electrolytic cell were put 100 pipettefuls, 491.14 cc. or 527.51 grams nitric acid, containing 0.0124128 gram NO_3 per cc. The current passing through the cells released oxygen in the one and hydrogen in the other. The electrolyte was tested from day to day as follows:

(1). Measure the current.
(2). Stir the liquids thoroughly.
(3). Withdraw one pipetteful and titrate with barium hydroxide.
(4). Test for nitrous acid with iodised starch solution.
(5). Test for ammonia with known excess of barium hydroxide.

From the results of these measurements the accompanying curves were platted.

Curve of Current.

The *y*-axis indicates the quantity of current that has acted on 100 cc. of the electrolyte since the connection was first made, March 9, 1891; this quantity being easily determined by dividing the quantity of current that flowed through the liquid in either jar by a number that would reduce the liquid in that jar to 100 cc., the amount of liquid in either jar being always known.

The x-axis is on the scale of one day per two divisions; the y-axis is on the scale of 500 coulombs per division.

The curve approximates a straight line, showing that the flow of current was quite steady and that the conductivity has changed but slightly, if at all, except on the tenth day, when the curve bends abruptly upward, owing to a removal of 100 ohms resistance, which confirms the opinion that the conductivity did not change very much, as such a change in resistance produces a large change in the current. Although the current was steady and constant, the decomposition was accompanied by curious phenomena.

Had no action taken place within the liquid, two volumes of hydrogen should have escaped for one volume of oxygen, but for several days after the apparatus was put in order it was easily seen that the flow of oxygen was largely in excess. Within a few days, however, the flow of hydrogen had apparently increased to the proper proportions. These rates of flow continued with little or no change until the fifty-ninth day, when it was noticed that the flow of hydrogen had almost ceased, while the flow of oxygen seemed unchanged. From the fifty-ninth day to the eighty-fourth day—that of last observation—the flow of hydrogen was very small, at times only a very few pin-point bubbles arising. The oxygen flow decreased gradually, but at no time became as small as the hydrogen flow.

Particular attention is called to the fact that after the fifty-ninth day the flow of gases was largely increased when the liquids were agitated; especially is this true of the hydrogen. Within a few hours the flow decreased to the amount that was given off before the agitation.

The titration indicated that the oxygen-liquid increased in acidity and the hydrogen-liquid decreased.

Curve of Increase in Strength of Oxygen-Acid.

With the same time-ordinate as before, but with the y-axis representing the increase in the amounts of barium hydroxide required to neutralise the oxygen acid, the curve of increase in strength of 100 cc. of the oxygen-liquid was platted. The increase in strength is due to the concentration of the electrolyte, with the transference of the ions, thus continually forming more nitric acid; and possibly to the formation of orthonitric acid, H_3NO_4.

Ammonium salt in minute quantity was detected by test-paper;

the quantity seemed slowly to increase, but at no time exceeded a trace. The presence of ammonium salt in this cell is probably due to the mixing of the liquids through the connecting-tube, thus introducing the salt from the hydrogen cell. The presence of nitrous acid (HNO_2) was not detected. The curve shows that the increase in strength has been slow but constant; the removal of the 100 ohms resistance the tenth day may be the cause of the more rapid increase in strength of the acid.

Curve of Decrease in Strength of the Hydrogen-Acid.

With the same ordinate as before, the curve showing the decrease in strength of the hydrogen-acid was platted, with the y-axis representing the amount of barium hydroxide required to neutralise 100 cc. of the liquid. The decrease in strength is due to decomposition of the electrolyte with transference of the ions and to the formation of ammonium salt. The ammonia steadily increased, but at no time was present in such quantity that it could be determined quantitatively. Owing to the formation of the ammonium salt and the transference of the ions, the hydrogen-liquid decreased in acidity more rapidly than the oxygen-liquid increased. The rapid descent of the curve after the tenth day is probably due to the removal of the 100 ohms resistance.

The curve of increase and the curve of decrease begin at the same point—the amount of barium hydroxide required to neutralise 100 cc. of the electrolyte before the current was started. The y-axis is platted on a scale of 5.5 cc. of barium hydroxide per division. The x-axis of each curve is platted on the scale of one day per two divisions.

The barium hydroxide used throughout this experiment was of such strength that 1 cc. equaled 0.9616 gram NO_3.

Curve of Ammonium Salt.

This curve, too, is platted for 100 cc. of the electrolyte with the same time-ordinate as before and the y-axis for milligrams NH_4, 5.5 milligrams per division. Assuming that the increase in strength would have equaled the decrease, but did not because of the formation of ammonium salt, the barium hydroxide required to neutralise 100 cc. of the oxygen-liquid is added to that required to neutralise 100 cc. of the hydrogen-liquid; the result is divided by 2 and the quotient subtracted from 1094, the number of cc. of

barium hydroxide required to neutralise 100 cc. of either acid at the beginning of the experiment. This difference is the amount of barium hydroxide that would have been required to neutralise the amount of nitric acid that had been neutralised by the formation of ammonium salt and also that consumed in the production of ammonia.

At the first the curve dips down, but soon turning upward proceeds in an irregular manner.

The peculiar action at the hydrogen-electrode since the fifty-ninth day indicates that important results would be reached by continuing the experiments, but the close of the session stopped further work.

The liquids then stood as follows: the oxygen-liquid had a specific gravity of 1.079 at 27° C., the hydrogen-liquid a specific gravity of 1.034 at 27° C.: at the beginning the specific gravity of the nitric acid was 1.069 at 20° C. The hydrogen-liquid decreased rapidly but regularly in strength; ammonium salt was formed slowly but with increasing rapidity in the hydrogen-liquid. Hydrazoic acid was not found.

The oxygen-liquid increased in strength very slowly, but no other change was observed. The quantity of ammonium salt was so small that all of it was probably brought from the hydrogen cell by the currents of liquid.

STATE UNIVERSITY OF MISSOURI, *June*, 1891.

NOTE ON THE ELECTROLYTIC DETERMINATION OF METALS AS AMALGAMS.

BY WOLCOTT GIBBS.

In a paper read before the National Academy of Sciences, in October, 1883, I gave an account of a method of electrolysis for the separation of metals from their solutions by the employment of metallic mercury as negative electrode, the positive electrode being a plate of platinum. Under these circumstances and with a current of moderate force I found it possible to separate iron, cobalt, nickel, zinc, cadmium and copper so completely from solutions of the respective sulphates that no trace of metal could be

detected in the liquid. In addition I found that phosphates of these metals dissolved in dilute sulphuric acid were easily resolved into amalgams and free acid, and I pointed out the advantage of the method in at least a certain number of cases. The process attracted the attention of chemists who were present at the meeting and was noticed in several of the daily papers. It was also noticed in the Zeitschrift für Analytische Chemie **22**, 558, and in the Chemical News **42**, 291. I had in view both the determination of the metal by the increase in weight of the mercury, and in particular cases of the molecule combined with the metal, either by direct titration, or by known gravimetric methods. It is but just to those chemists who have since studied the method to state that my experiments were purely qualitative, such being in my opinion sufficient to establish the correctness of the principle involved.

The method is described in Prof. Edgar F. Smith's work[1] on electro-chemical analysis, but it is incorrectly stated that it was applied to tin and mercury. I made no experiments with either tin or mercury. In 1886, two years after the presentation of my paper to the National Academy, Luckow[2] applied the same process to the estimation of zinc. Very recently Prof. T. M. Drown[3] has shown that the quantitative separation of iron from even very small quantities of alumina may be effected by electrolysis with mercury, the results being very satisfactory. It is to be expected that the process will give equally good results in the separation of iron and some other metals from titanium, zirconium, niobium and tantalum.

Very recently the subject has been taken up by Vortmann,[4] who has made numerous quantitative experiments with mercury, zinc, cadmium, lead, bismuth and antimony. The numerical results obtained, if not extremely accurate, are at least fairly good. It is to be hoped that the determination quantitatively of the electro-negative atoms or molecules united with the metal will also attract attention, the method having been originally intended to serve the double purpose. The inaccurate statements which have been made as to my own share in the invention of the process have led to the publication of this note.

NEWPORT, R. I., *Nov.* 1, 1891.

[1] Electro-chemical Analysis, by Edgar F. Smith. Philadelphia, 1890.
[2] Ztschr. anal. Chem. **25**, 113, 1886.
[3] Transactions of the Institute of Mining Engineers **20** (not yet published), 1891.
[4] Ber. d. chem. Ges. **24**, 2749.

SAPOTIN: A NEW GLUCOSIDE.

By Gustave Michaud.*

Achras Sapota, L., is a large tree scattered through the forests of Central America and the West Indies; its fruit is often seen upon the Creole dinner-table. This fruit is a berry, the size of an orange, the taste of which suggests the flavor of melon, as well as that of hydrocyanic acid. The fruit contains one or two seeds like large chestnuts, which if broken let fall a white almond. This last contains the glucoside which I call *sapotin*.

I obtained sapotin for the first time by heating dry raspings of the almond with 90-per cent. alcohol. While cooling, the filtered liquid deposited a good deal of the compound. Since that time I have advantageously modified the process and increased the amount of product. I prepare sapotin in the following way: The almonds are rasped, dried at 100° C. and washed with benzene, which takes away an enormous quantity of fatty matter. The benzene which remains in the almond is driven out first by compression, afterwards by heating. Then the raspings are exhausted with boiling 90-per cent. alcohol. The solution is filtered as rapidly as possible, in order to avoid its cooling and depositing the sapotin in the filter. As soon as the temperature of the filtered liquid begins to fall, a voluminous precipitate is seen to form, which is the sapotin.

In order to purify it, the precipitate is collected in a filter and expressed between sheets of filter-paper. When dry it is washed with ether, which takes away the last particles of fatty and resinous matter. The purification is completed by two crystallisations from 90-per cent. alcohol. At last the substance is dried at 100°.

The sapotin separates from its alcohol solution in the form of microscopic crystals. When dry, it is a white, inodorous powder. Its taste is extremely acrid and burning. If the powder penetrate into the nostrils or the eyes it produces a persistent burning sensation which brings about sneezing and flow of tears. It melts at 240° C., growing brown at the same time.

It has a laevo-rotatory power of $[\alpha]_j = -32.11$, which was determined with an alcoholic solution, the aqueous solution not being sufficiently transparent.

It is very soluble in water, easily soluble in boiling alcohol, much less in cold alcohol, and insoluble in ether, chloroform and benzene. Its alcoholic solution is precipitated by ether.

Tannin has no action on it, but basic acetate of lead produces a gelatinous precipitate in its aqueous solution. Strange enough, this precipitate is entirely soluble in a small excess of basic acetate of lead. If thrown into concentrated sulphuric acid, sapotin colors it with a garnet-red tint. It does not reduce Fehling's solution. Its analysis gave the following results:

	Calculated for $C_{29}H_{52}O_{20}$.	Found. I.	II.
C	48.33	48.69	48.31
H	7.23	7.33	7.45

When heated with water and a little sulphuric acid, sapotin is decomposed and yields glucose and an insoluble matter which I call *sapotiretin*. 100 parts of sapotin produce 51.58 parts of glucose and 49.67 of sapotiretin. The equation which represents this reaction is—

$$C_{29}H_{52}O_{20} + 2H_2O = 2C_6H_{12}O_6 + C_{17}H_{28}O_{10},$$

and requires 50 per cent. of glucose and 55 per cent. of sapotiretin.

Sapotiretin is an amorphous compound, insoluble in water, very soluble in alcohol, less soluble in chloroform, insoluble in ether. Below is the result of its analysis:

	Calculated for $C_{17}H_{32}O_{10}$.	Found. I.	II.
C	51.52	51.21	51.20
H	8.08	8.19	8.34

REVIEWS AND REPORTS.

STEREOCHEMISTRY.

(*Continued from* p. 504.)

The "Strain" Theory of Von Baeyer.

A striking characteristic of Van't Hoff's explanation of the isomerism described at the close of the first part of this paper[1]

[1] This Journal **13**, 503.

is the spontaneity with which that explanation flows from the original Tetrahedron Hypothesis. With equal readiness does this hypothesis lend itself—as was first shown by Van't Hoff—to the explanation of ring-formation and the superior stability of rings of five or six carbon-atoms. Later Von Baeyer[1] attempted a similar explanation, adding this hypothesis: "The four valences of a carbon-atom act in the direction of the lines connecting the center of a regular tetrahedron with the apices, lines which are at an angle of 109° 28′ with one another. The direction of the attraction can undergo a divergence, which, however, is attended by a proportional strain." In acetylene, *e. g.*, the three valences connecting the carbons are all diverted from *Ca* to *CC* (Fig. 9); hence

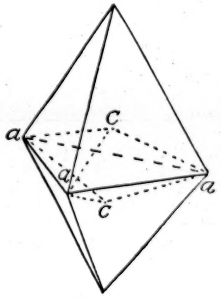
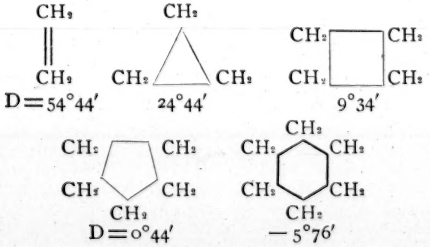


FIG. 9.

the negative heat of formation of acetylene, and the explosive nature of its compounds, and especially of polyacetylene compounds. The greater the divergence, the greater the strain; the greater the strain, the less the stability. Of the different methylene-rings the five and six carbon-rings show the least divergence (*D*) of their valences from the angle 109° 28′.



[1] Ber. d. chem. Ges. **18**, 2277.

In these, then, the strain is least, and therefore it is that they are the most stable. Moreover, König[1] maintains that the pentamethylene is more stable than the hexamethylene ring.

Naumann[2] has given an explanation of the weakness of the triple- and double-bonds which differs from that of Von Baeyer. He supposes that of the affinity-force directed towards the corners of two carbon-atoms, only the component which acts in the line joining the tetrahedron-centers is effective in holding the two atoms together. Calling this for $\overset{C}{\underset{C}{|}} = 1.0000$, it will be for $\overset{C}{\underset{C}{||}} = .5774 \times 2$ and for $\overset{C}{\underset{C}{|||}} = .3333 \times 3$. The force required to break one bond will be, then, for $\overset{C}{\underset{C}{|||}} > .3333$, for $\overset{C}{\underset{C}{||}} > .5774$, and for $\overset{C}{\underset{C}{|}} > 1$.

Von Baeyer[3] rejects this explanation, saying that the affinities may be represented by elastic wires, the bending of which causes a strain not taken into account by resolving the attractive force according to the parallelogram of forces. The "strain" theory also has been criticised.[4] In fact, according to the valence hypothesis of V. Meyer and Riecke,[5] it is unnecessary to assume a divergence of valences in acetylene. Besides, we can form in connection with the mutual attraction of atoms no conception of that which corresponds to Von Baeyer's elastic wires.[6]

The Theories of Wunderlich and of Skraup.

A mode of representing the linkage of carbon-atoms which is free from the objections just mentioned is given by Wunderlich.[7] It is based on an hypothesis as to the form of the carbon-atom. Van't Hoff had offered no suggestion as to this; with him, the tetrahedron is merely the form enclosed by lines joining the points which radicles attached to a carbon-atom occupy relatively to one another. Wislicenus[8] thinks it possible that this tetrahedron represents the form of the carbon-atom, the attractive force of the atom being concentrated at the apices; so that where there is least matter there is most force. Wunderlich, however, conceives the atom as having at least some matter round its binding-points, probably as much as anywhere else; so that the atom may be spherical, *e. g.*; or the atom-substance may be concentrated

[1] Chem. Centrbl, 1890, **1**, 788.
[2] Ber. d. chem. Ges. **23**, 477.
[3] Ber. d. chem. Ges. **23**, 1272.
[4] Ibid. **23**, 581.
[5] Ibid. **21**, 949.
[6] Comp. Auwers, "Entwicklung der Stereochemie" (Heidelberg, 1890), pp. 18 and 25. See also p. 152, where V. Meyer gives reasons for doubting whether the double and triple bonds are really weaker than the single bond.
[7] "Configuration organischer Moleküle" (Würzburg, 1886); or see Auwers, "Entwicklung," pp. 18 *et seq.*
[8] Ber. d. chem. Ges. **21**, 584.

behind the binding-points so that the form of the atom may be a regular tetrahedron, but with the binding-points in the centers of the faces. The atom-form would be represented in the former case by the sphere, in the latter by the tetrahedron circumscribed about the tetrahedron of Van't Hoff or Wislicenus. In any case—and this is the essential hypothesis—the atom-substance is conceived as so disposed between the binding-points that the single-link between two carbon-atoms is the only connection permitting of actual contact of binding-points. Let us consider, for example, the tetrahedra of Wunderlich. Singly-linked, these would be face to face, two binding-points would touch; doubly-linked, they would have two pairs of faces opposed or would be edge to edge; trebly-linked, three faces of one would be opposed to three of the other, or the tetrahedra would be point to point. Assuming these positions, and that the attraction varies inversely as the square of the distance between the binding-points concerned, Auwers[1] calculates the ratio of the strength of the double-link to that of the triple-link to be 3.56 : 1. If the atoms are not tetrahedra, but spheres, the ratio is 1.65 : 1.

When the tetrahedra of Wunderlich form saturated rings, the singly-linked faces can no longer touch; their angle of inclination is least for five-carbon rings, and increases as the number of carbon-atoms differs from five; so that here too we have a very simple representation of the facts.

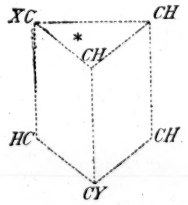
Again, since in the doubly-linked tetrahedra the binding-points do not touch, oscillations causing them to approach and recede are possible. Suppose such oscillations to take place in the plane of the four binding-points concerned. Then atoms capable of forming an addition-product will attach themselves to the binding-points which have receded, and are therefore now less nearly saturated; the approaching points continuing to approach till they touch; *i. e.*, addition of elements to doubly-linked carbons will usually break one bond, not both, as would be the case if the two were permanently equal. But owing to the oscillations, addition is as likely to take place on one side of a molecule as on the other; *i. e.*, from fumaric acid we get as many molecules of right- as of left-handed tartaric acid, not all right- or all left-handed acid, as would be the case if the two bonds were permanently unequal. This ingenious modification of Wunderlich's conception is due to Skraup.[2] One comment may be permitted: the oscillations assumed involve recession of the two binding-points which have approached (whose attraction should therefore be increased), and approach of the two binding-points on the other side which have receded (whose attraction should therefore be diminished). Thus the oscillation-hypothesis is in conflict with the hypothesis that the attraction between two binding-points increases as the distance between them diminishes.

[1] "Entwicklung," p. 33.

[2] Monatsh. Chem. 12, 146.

The Configuration of the Benzene Molecule.

The discussion of this problem has involved the application of most of the theories which have been sketched. The later theory of Van't Hoff, that every *C* group is optically active, has been used to determine the choice between conflicting benzene formulæ. If two ortho-hydrogens in benzene are replaced by different radicles, we have, according to the prism-formula, an asymmetric carbon-atom (marked *).



But no substitution-product of benzene is active, nor has any been rendered active even by the action of ferments. The preference must therefore be given to a formula like that of Kekulé, showing the carbons with double-bonds or with central valences. Such a formula is in accordance with the fact that only addition-products of benzene are active.

An attempt has been made to apply also the theory peculiar to Le Bel. Since, according to this, *any* asymmetric molecule is active, every benzene derivative in which three hydrogens are substituted should, it is said, be active unless these hydrogens occupy a plane of symmetry of the molecule.[1] The absence of active substituted benzenes proves, therefore, that all the hydrogens are in a plane of symmetry of the molecule. According to Van't Hoff,[2] it proves also that all the carbon-atoms are in the same plane. Herrmann,[3] however, does not regard this as a necessary consequence. He gives a formula for benzene, in which the six carbons are divided into two groups, occupying two planes parallel with the plane of the hydrogen-atoms and equidistant from it.

No carbon-atom of one group is opposite a carbon-atom of the other; but the centers of gravity of the two groups are opposite and balance one another about the central plane containing the

[1] This reasoning, however, like that by which the formula for methane was deduced, is based on the unproved assumption that the radicle substituted for a hydrogen-atom takes the place previously occupied by that atom.
[2] Loc. cit. p. 81.
[3] Ber. d. chem. Ges. **21**, 1958.

hydrogen-atoms. Thus any optical activity due to one of the groups will be counterbalanced by the opposite activity of the

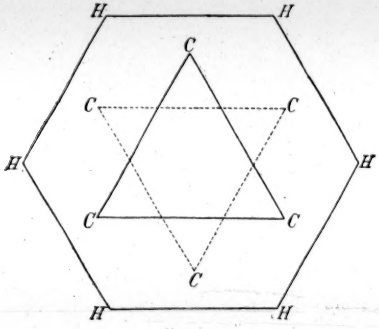
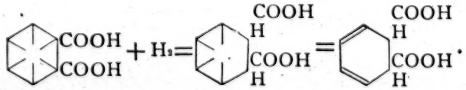


FIG. 10.

opposite group. Von Baeyer's investigation of the constitution of benzene—a result of his strain-theory—led him to the space-formula shown in the figure[1] (Plate I). The formula had already been proposed by Armstrong.[2] It is the ground-plan of the other with the middle left out, and both are intended to show that no one of the central valences monopolises any other, but all "mutually paralyse one another" (Von Baeyer). The valences are potential, not active. The linking of the carbon-atoms is stronger than any that exists in rings without central valences, and as Bamberger[3] shows for aromatic rings in general, the difference ceases directly the equilibrium of the central valences is disturbed by formation of addition-products. The potential valences become active. For instance, in the reduction of phthalic acid,



See Plate I.[4]

[1] Loschmidt (Monatsh. Chem. **11**, 28) reproduced this formula two years later to account for the formation of benzene from acetylene.

[2] J. Chem. Soc. **51**, 264.

[3] Ann. Chem. (Liebig) **257**, 1 (1890). The theoretical conclusions of the paper had been to a large extent anticipated by Marsh (Phil. Mag. 1888, **2**, 426).

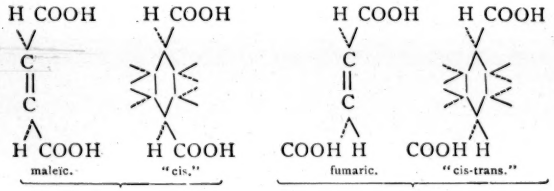
[4] The formula given probably represents not the existing dihydro-phthalic acid, but an isomer. (Von Baeyer, Ann. Chem. **258**, 160.)

PLATE I.

H
H
H

In opposition to the central formula, Ladenburg[1] maintains that it lacks a mechanical basis; that the valences of two diagonally opposed carbons being equal and opposite, must mutually saturate each other, so that no part of their attractive force can be engaged with any other central valence; but this is saying that each pair of diagonally opposed carbons is linked in the ordinary way, *i. e.*, that the central formula is equivalent to Claus's diagonal formula.

A remarkable link between the stereochemistry of rings and that of the double-bond was found by Von Baeyer in the two hexahydro-terephthalic acids, called by him "cis" and "cis-trans." In appearance and in solubility these acids mimic maleïc acid and fumaric acid respectively; moreover, the less stable maleoid acid readily passes into the more stable fumaroid acid. The analogy is completely represented by the formulæ[2]



and was foreseen by Van't Hoff in 1875.

Sachse[3] objects to these formulæ that they do not account for the conversion of "cis" to "cis-trans" acid *in the cold*, and he suggests another space-formula for hexamethylene, which is easily derived from his formula for benzene;[4] and Herrmann[5] protests against all attempts to arrive at the formula of hexamethylene or of benzene by the placing together of tetrahedra, and points to the impossibility of representing the formation of benzene from acetylene by a multiplication of the space-formula of the latter.

[1] Ann. Chem. (Liebig) **246**, 382; Ber. d. chem. Ges. **23**, 2688. Compare also Claus: J. prakt. Chem. [2] **40**, 69, and **42**, 24; and Von Baeyer's answer to him: Ann. Chem. (Liebig) **258**, 145; also Bamberger's: J. prakt. Chem. [2] **42**, 188.

Wachter (Chem. Centrbl. 1890, **1**, 457 has given a compact review of the evidence for the various benzene-formulæ, including the space-formulæ.

[2] The dotted lines are supposed to be on one side, the corresponding solid lines on the other side of the plane of the ring. Other cases of this isomerism are the benzene hexachlorides (Friedel: Bull. Soc. Chim. [3] **5**, 130; abstract: This Journal **13**, 356), the thioaldehydes (Baumann: Ber. d. chem. Ges. **24**, 1419, compare Figs. 45 and 46 in Van't Hoff's "La Chimie dans l'espace." 1875); and the menthols (Beckmann: Ann. Chem. (Liebig) **250**, 322). See also p. 87 of "Chemistry in Space," a translation by Marsh of the "Dix Années," with additions by Van't Hoff (Oxford, 1891, Clarendon Press).

[3] Ibid. **23**, 1363.

[4] Ibid. **21**, 2530; abstract: This Journal **11**, 132. Compare, however, Herrmann: Ber. d. chem. Ges. **23**, 2060, and Auwers, "Entwicklung," p. 51.

[5] Ber. d. chem. Ges. **23**, 2060.

Development of the Theory concerning Unsaturated Isomers by Wislicenus.

The explanation of isomerism of the fumaric-maleïc type, resulting from the space-formula for ethylene, though published by Van't Hoff in 1874, began to hold and dominate chemical thought on these subjects only when, in 1887, the work of Wislicenus[1] rendered the theory amenable to the test of experiment. Hence much of Van't Hoff's theory is sometimes[2] ascribed to Wislicenus. And this is not remarkable, since the ideas of Wislicenus grafted themselves so naturally on the theory of Van't Hoff, and the offshoots of both are so intricately interlaced, that it is difficult to distinguish at all points between the earlier and the later growth. For Wislicenus introduced but one additional hypothesis, and with the further aid of one simple and well-recognised principle he then followed out logically and applied systematically the hypotheses of Van't Hoff. Van't Hoff had said that two trebly-linked carbons are represented by two tetrahedra face to face. Wislicenus said: It follows that any two monad radicles added to these will be on the same side of the molecule.

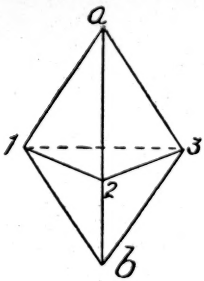


FIG. 11.

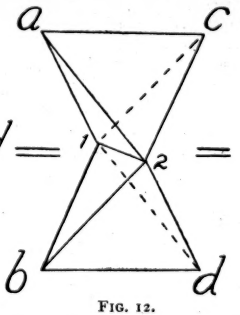


FIG. 12.

The principle here is that of least disturbance: no more bonds are to be broken than is necessary to effect the transformation. The same principle was applied to the change from the double to the single bond. Again, Van't Hoff had said that two carbon-atoms singly-linked might rotate in opposite directions round the axis joining their centers, but for the fact that they are held in one position by the affinity of the groups attached to the one

[1] "Ueber die räumliche Anordnung der Atome in organischen Molekülen und ihre Bestimmung in geometrisch-isomeren ungesättigen Verbindungen." Leipzig, 1887; 2d ed. 1889.
[2] Compare, *e. g.*, Pattison Muir, loc. cit. pp. 182 and 183.

for the groups attached to the other; the position of equilibrium depending for each compound on the nature of the groups, and being left undetermined. Wislicenus said that with the aid of

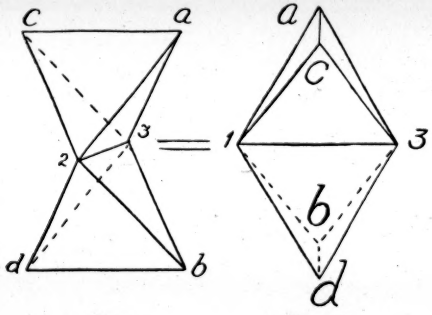


FIG. 13. FIG. 14.

the hypothesis that the greater the difference in "positivity" or "negativity" the greater the affinity between two radicles, we could for many compounds determine the position of equilibrium. Thus of the three configurations for malic acid the third is the

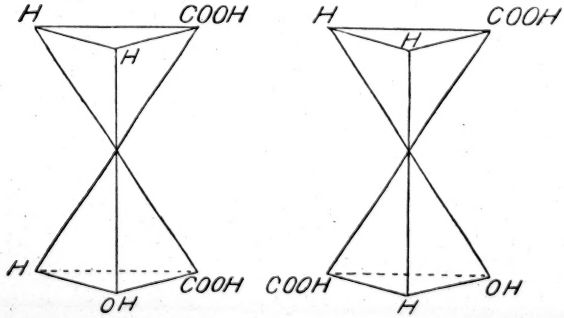


FIG. 15. FIG. 16.

stable configuration, and the other two, if formed, would immediately by rotation be converted into it. But this state of affairs may be modified by the atomic motion due to heat, until at a

sufficiently high temperature all the relative positions possible for the radicles H, H, COOH with regard to H, OH, COOH, may be realised successively at equal intervals of time. As Van't Hoff

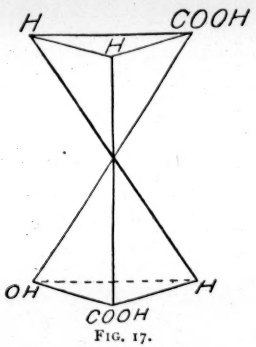
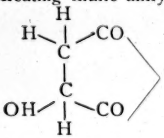


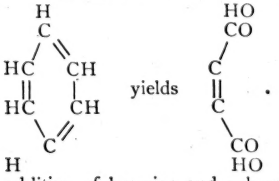
FIG. 17.

observes with regard to the way in which the validity of inferences from the theory may be affected by the action of heat: "Throughout, our theory can represent the reality only as this would be at absolute zero" (p. 88).

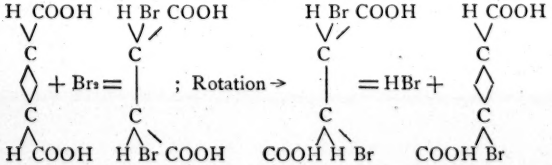
In the case of the formation of a non-saturated from a saturated compound, we are aided in fixing the position of our six radicles by the fact that the two radicles leaving the molecule—the two whose simultaneous action causes the change—must be opposite to each other—in "corresponding positions"—at the moment of the change. This necessity and the affinities of the radicles of the saturated compound often indicate the position of the radicles in the unsaturated compound formed. It was the positions of the radicles in unsaturated isomers which Wislicenus wished to determine, and we can best illustrate his theories and those of Van't Hoff by applying them to two ethylene derivatives—

fumaric and maleïc acids, $\begin{matrix}CH\ COOH\\ \|\\ CH\ COOH\end{matrix}$. From what has been said it follows—(1), that the acid formed by the addition of Br_2 to $\begin{matrix}C\ COOH\\ |||\\ C\ COOH\end{matrix}$ will have both the carboxyls on the same side; (2), that the acid in which both the carboxyls are on the same side will be the less stable. Moreover, (3), this acid only can have an anhydride, $\begin{matrix}HCCO\\ \|\\ HCCO\end{matrix}\!>\!O$. The facts are in accord with

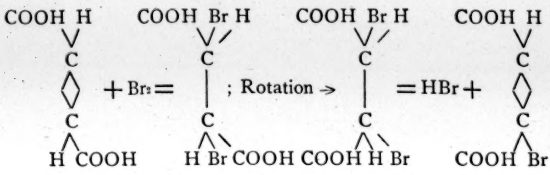
these demands of the theory; it is the same acid which is formed in (1), which is the less stable (2), and which has the anhydride (3); in every case it is maleïc acid[1] . Further, it is fumaric acid, , that is formed by the splitting off of water from malic acid at 150°, because the favored configuration of malic acid is . But it is maleïc acid that is formed by heating malic anhydride which can have only the configuration  In the slow oxidation of benzene it is—as the formulæ demand—maleïc acid which is formed:



Further, the addition of bromine and subsequent removal of hydrobromic acid converts maleïc into bromo-fumaric acid, and fumaric into bromo-maleïc acid,



[1] Bandrowski found dibromo-fumaric acid to be formed by addition of bromine to ; but Wislicenus showed that this was a secondary product, dibromo-maleïc acid being first formed.



These transformations can be properly represented only by models (solid formulæ); the formulæ given must be imagined solid.

In substances of the maleïc type (Fig. 18), like radicles have positions symmetrical with regard to a plane passing through the common edge at right angles to lines joining *aa* and *bb*. These substances are therefore called plane-symmetrical. Similarly, substances of the fumaric type (Fig. 19) are called center-symmetrical; or we may call them axis-symmetrical; the line of contact being the axis of symmetry.[1]

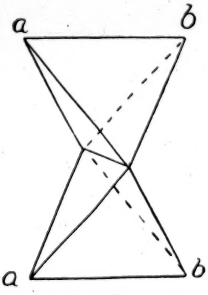


FIG. 18.

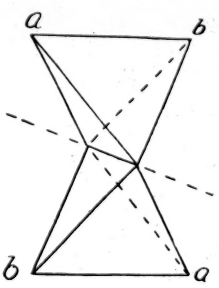


FIG. 19.

The stereochemical explanation of the isomerism of fumaric and maleïc acids has met with objections on the part of Michael[2] and of Anschütz,[3] "among which," says Victor Meyer,[4] "*one* may indeed be considered serious." Wislicenus had explained the ready transformation of maleïc into fumaric acid in the presence of hydrobromic acid, hydrochloric acid, etc., by the hypothesis

[1] In Wislicenus' treatise the axis of symmetry is incorrectly represented as in Fig. 20. The term center-symmetrical is preferred in the second edition.
[2] J. prakt. Chem. (2) **38**, 21.
[3] Ann. Chem. (Liebig) **254**, 168. Compare also Fittig: Ibid. **259**, 1.
[4] Ber. d. chem. Ges. **23**, 586.

that an addition-product was formed, that the now singly-linked carbon-atoms rotated until the most stable configuration was reached, and that then the added atoms again split off, leaving the more stable acid.

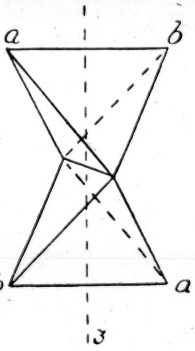


FIG. 20.

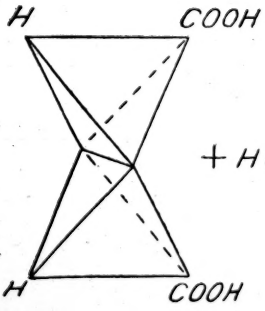


FIG. 21.

+ HCl =

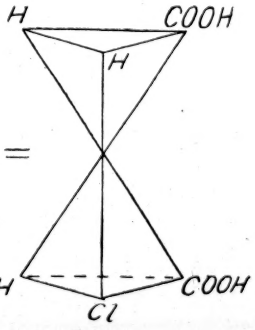


FIG. 22.

It was objected that only on boiling does the addition-product chlor-succinic acid give up hydrochloric acid and yield fumaric acid; whereas the transformation in question takes place at 10°. Whereon Victor Meyer remarks: "Wislicenus has not

to my knowledge been able to dispose of this objection in a satisfactory way." The explanation given by Van't Hoff[1] was, however, never open to this objection. The transformation involves

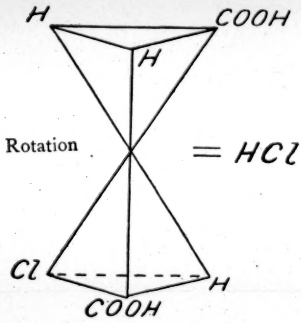


FIG. 23.

$= HCl +$

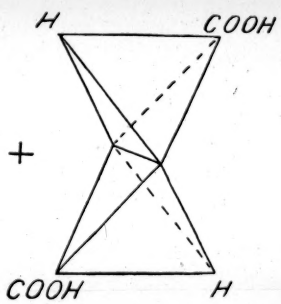


FIG. 24.

separation and then rotation of the four linked tetrahedron-corners. Now, addition also involves, as a necessary preliminary, separation of one pair of linked corners; but the symmetry of the maleïc acid molecule will cause both sides of it to be acted on alike; therefore *both* pairs of linked corners will be separated. So that before any addition has taken place the tetrahedron-corners will be on the way to their new positions.[2] This theory reminds us of the experiments of Morse and White,[3] showing that the dissociation of a compound AB is favored by the presence of a substance C capable of combining with A or B.

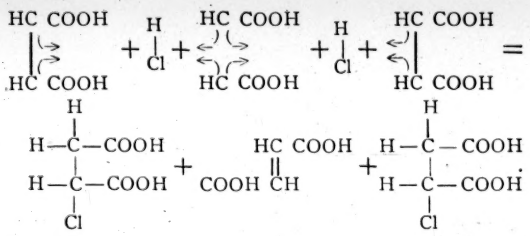
$$\begin{matrix} A \\ B \end{matrix} + C = A + B + C; \qquad \begin{matrix} HC\ COOH \\ \| \\ HC\ COOH \end{matrix} + C = \begin{matrix} HC\ COOH \\ \diagup\!\diagdown \\ \cdots\cdots \\ \diagdown\!\diagup \\ HC\ COOH \end{matrix} + C.$$

The explanation of both cases of dissociation is perhaps analogous to that given by Ciamician[4] for the dissociation of electrolytes by water:

$$\underset{+\,-}{AB} + \underset{+\ -}{H_2O}\,(q.\,s.) = H_2O\,A\begin{matrix} H_2 \\ O \\ O \\ H_2 \end{matrix} + OH_2\,B\begin{matrix} O \\ H_2 \\ H_2O \\ O \end{matrix} + xH_2O.$$

[1] L. c. p. 90.
[2] Bischoff also is of opinion that no actual addition takes place, and has supported this opinion by experiments.—Ber. d. chem. Ges. **23**, 1925.
[3] This Journal **11**, 260.
[4] Ztschr. phys. Chem. **6**, 403.

"Failure of C to maintain the dissociated condition of A and B might result from a lessening of its relative quantity." (Morse and White.) *E. g.*



Thus the formation of an addition-product would favor the transformation of molecules not directly affected by the addition. But addition does not seem to be essential. The attraction of a substance capable of forming addition-products may suffice to destroy the equilibrium of the less stable molecule HCCOOH ‖ HCCOOH and yet not suffice to prevent the formation of the more stable molecule HCCOOH ‖ COOHCH[1]. This, the explanation of Van't Hoff, accounts for the transformation effected by traces of bromine or iodine, and seemed to be the most generally applicable hypothesis. But the researches of Skraup[2] conducted especially with a view to determine the conditions necessary for the conversion of maleïc to fumaric acid, show that the conversion takes place not only when there is no addition, but when there is probably no tendency to the formation of addition-products. Skraup is convinced that conversion is the catalytic accompaniment of certain chemical actions; that oscillations[3] of the binding-points in the direction of conversion characterise the double-bond, and that these may be reinforced by neighboring oscillations of the proper pitch produced by chemical action between other bodies, until, the upper and lower halves of the molecule each swinging through 90° in opposite directions, an interchange of binding-points takes place.

This discussion illustrates the elasticity of stereochemical theory with regard to these transformations—an elasticity which

[1] Compare Grubler's analogy quoted by Bischoff (*l. c.*): "A piece of iron alters the direction of a magnetic needle from afar, but holds the needle fast only when in immediate contact with it."

[2] Monatsh. Chem. **12**, 107.

[3] Compare *ante* p. 576. The planes in which these oscillations take place are at right angles to the plane of the oscillations there described.

makes it impossible to crush the theory by the pressure of facts bearing on isolated points, but indicates at the same time a vagueness which only future experiments can diminish. Meanwhile the contest[1] between Wislicenus and his opponents continues.

ARNOLD EILOART.

[*To be continued.*]

NOTE.

The Preservation of the Alkali Metals.

M. Rosenfeld[2] describes a method for removing the crusts of hydroxide from metallic sodium, potassium and lithium, and for keeping these metals bright. Bring the metal into a mixture of one part of amyl alcohol and three parts of petroleum, and with a rag rub it under the liquid till it is silvery white. Put it for a few minutes in petroleum containing 5 per cent. of amyl alcohol; then wash it thoroughly with pure petroleum. Finally, preserve it under petroleum to which from 0.5 to 1 per cent. of amyl alcohol has been added. The metal remains bright under these conditions for a long time, but finally becomes covered with a coating of amylate, which is, however, easily removed by rubbing with filter-paper.

E. R.

[1] Wislicenus: Ann. Chem. (Liebig) **246**, 53; compare Fittig's reply; Ibid. **259**, 1. Blank: Ibid. **248**, 1. Wislicenus: Ibid. **248**, 281. Compare Michael's reply: J. prakt. Chem. [2] **40**, 29. Wislicenus: Ann. Chem. (Liebig) **250**, 224. Compare the reply of Favorsky and Debout: J. prakt. Chem. [2] **42**, 149.

[2] Ber. d. chem. Ges. **24**, 1658.